CHAPTER 18

ESTUARIES

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Contents

1. INTRODUCTION

In the first edition of this book, Nixon and Pilson (1983) began their chapter on nitrogen in estuaries by indicating it was an exciting and challenging time to be engaged in such studies. In the two decades since, that assessment continues to apply. In fact, studies of nitrogen (N) in estuarine ecosystems have so greatly expanded, intensified, and diversified that it is a challenge to capture even highlights of progress in this hyperactive area of research.

Nitrogen in the Marine Environment

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Why have so much intellectual and other forms of capital been devoted to understanding N in estuarine ecosystems? A case can be made that a central work stimulating N investigations in estuarine systems was Ryther and Dunstan's (1971) paper in Science where they concluded, based on nutrient ratios and bioassay experiments, that N rather than P limited coastal algal growth and eutrophication and that reductions in P inputs to these systems would have little restorative effect. Prior to this, and for many subsequent years in some regions of the world, it was generally believed that P limited primary production, if indeed any essential element was limiting in estuaries. In a limited number of estuaries it was known that relatively large loads of N and P entered these systems. However, light was often thought to be limiting in typically turbid estuarine waters and short water residence times (compared to many lakes) were believed to rapidly transport nutrients from estuaries before biota could make use of these compounds (e.g., Schindler, 1981). A decade later the book Estuaries and Nutrients appeared (Neilson and Cronin, 1981) and for the first time there was a broad examination of nutrients in estuarine ecosystems. Papers included reviews and a few syntheses (e.g., Nixon, 1981), case studies from a limited number of estuarine ecosystems, and a few examples of estuarine responses to nutrient management efforts (Jaworski, 1981; Smith, 1981).

By the early to mid-1980s it became increasingly clear to many government agencies and environmental advocacy groups that something was seriously wrong with some estuarine systems (e.g., D'Elia *et al.*, 2003; Malone *et al.*, 1993). During this time several of the large estuarine restoration programs began in such sites as Long Island Sound, Chesapeake Bay, Tampa Bay and San Francisco Bay. With these programs came ambitious monitoring efforts where nutrient inputs from major rivers were gauged, point sources of nutrients were documented and estuarine nutrient concentrations, as well as other chemical (e.g., dissolved oxygen) and biological (e.g., chlorophyll *a*) variables, were routinely measured, often at many sites. A real estuarine data avalanche had begun and continues today; however, it also appears that many of these data sets remain severely under-analyzed. Bricker *et al.* (1999) produced a qualitative evaluation of water quality and habitat conditions in USA estuaries that included some 143 systems, again indicating the broad distribution of activities in these ecosystems. This trend has included sharp increases in the number of reported rate measurements and associated improvements in measurement techniques including measurements for rates of nutrient inputs to estuaries, primary production, denitrification rates, sediment-water exchanges of N, P and C, deposition of organic matter, burial of particulate nutrients, and others.

Given two decades of measurement frenzy since 1984, some have asked, what does all this mean? Are these systems all different or do they share some fundamental similarities? Do they respond to N loads in some understandable fashion, are internal losses of N proportional to loads and are there estuarine features that regulate the magnitude of N export to the coastal ocean? How do nutrients shape the structure and function of estuarine food-webs? There is an emerging, and hopefully accelerating, pattern of estuarine data synthesis taking place and N plays a prominent role in these efforts. Early work along these lines (e.g., Boynton *et al.*, 1982; Nixon, 1981) indicated the importance of N in regulating algal primary production and biomass, and Nixon substantially expanded comparative estuarine analyses to include aspects of nutrient cycling (Nixon, 1981) and secondary production (Nixon, 1982, 1988, 1992). Monbet (1992) related algal biomass in a large number of European estuaries to N concentrations after classifying sites according to tidal range. More recently, nutrient budgets have been used as a quantitative framework to organize diverse data sets towards testing our understanding of N dynamics at the level of whole ecosystems (e.g., Boynton *et al.*, 1995; Nixon *et al.*, 1996; Wulff *et al.*, 1990).

Degradation of estuarine environments prompted much of the interest in estuarine research and it now appears that nutrient-based eutrophication has become a central estuarine research theme, just as it did in limnology where this theme had the effect of unifying theoretical and applied aspects of that discipline. In recent years several reviews and syntheses have appeared with eutrophication being the core issue and considerations of N playing a very prominent role. Kelly (2001) and Rabalais (2002) reviewed N effects on coastal marine ecosystems, Cloern (2001) proposed several versions of a new eutrophication conceptual model and Smith (2003) reviewed and compared eutrophication responses of primary producers in lake, reservoir, marsh and estuarine systems (see also Chapter 11 by Paerl and Piehler, this volume). While it is clear that much needs to be done, it is equally clear that understanding of N in estuarine ecosystems has improved during the two decades since publication of Nitrogen in the Marine Environment (Nixon and Pilson, 1983).

The goal of this chapter is to provide an overview of advances during the past 20 years in our understanding of N in estuarine ecosystems and to suggest some fruitful directions future research might take. We have taken advantage of recent reviews, added information to several existing syntheses and generated several new summaries and syntheses from the almost overwhelming amounts of estuarine N data available. Three data summaries were developed specifically for this paper and these included N and P concentrations in the water columns of a variety of estuaries (Frank *et al.*, 2007), aquatic denitrification rates (Greene, 2005a), and estuarine sediment-water solute fluxes (Bailey, 2005). In this review we have: (1) examined N concentrations from a wide variety of estuaries to describe distinct spatial-temporal patterns in relation to season and climate, (2) reviewed, compared and expanded reported N-budgets for estuarine systems, (3) compiled extensive data on sediment-water fluxes of N and other solutes and examined regulating factors, (4) summarized and compared annual patterns and rates of phytoplankton primary production in relation to nutrient limitation, and (5) reviewed current concepts concerning interactions between N and both trophic state and secondary production in estuaries.

2. DISTRIBUTION OF DISSOLVED NITROGEN IN ESTUARINE WATERS

During the last twenty years, water column concentrations of dissolved N were probably the most intensively measured feature of N in estuarine environments. For example, about 8000 measurements of each of the common dissolved N species (i.e., NO_2, NO_3, NH_4 and dissolved organic nitrogen) were made per year for the past twenty years as part of routine monitoring in Chesapeake Bay (Chesapeake Bay Water Quality Monitoring Program, 2004). Similar measurement programs have been gathering N concentration data for a decade or more (e.g., Danish estuaries, Conley *et al.*, 2000; Tampa Bay, Greening and DeGrove, 2001). In this section we review earlier efforts describing N distributions, provide some comparative analyses of N concentrations gleaned from examination of data compiled from many estuaries and conclude with a more detailed description of N distributions in Chesapeake Bay where these compounds have been measured at many sites and under variable climate conditions for several decades.

2.1. Previous examinations of nitrogen distributions

Earlier reviews of N distributions struggled to gather sufficient nutrient data to search for commonalities or differences among estuaries, but the current challenge is to organize the huge number of measurements into some tractable form. Given the enormous increase in the number of observations available, it's appropriate to ask what we have learned. Are there a limited number of N distribution patterns among estuarine systems or is variability in space and time the dominant feature? Estuarine characteristics such as river flow, depth, degree of stratification, water transparency, autotrophic community composition, and water residence time all influence N distributions. Since these characteristics vary widely both within and among estuaries we might expect reactive N-compounds to do the same.

Boynton *et al.* (1982) organized seasonal-scale dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP) data from 28 estuarine systems and reported that concentrations of DIN ranged from <1 to 60 μM at the time of the year when phytoplankton production was at a maximum (generally during summer). In addition, DIN: DIP ratios in 75% of these systems were less than 10 during the period of highest production, suggestive of N-limitation, although ratios varied widely during the year, especially in river dominated estuaries. Nixon and Pilson (1983) examined nutrient concentrations in more detail from about a dozen USA estuarine systems. They also noted an extreme range in N concentrations among estuaries (0.1 to >200 μM) and found estuaries where DIN was very depleted in the water column, always abundant, or seasonally variable; the limited data available in the early 1980s may have largely prevented finding clear patterns of N concentration among estuaries.

In a recent and comprehensive review of 81 Danish estuaries it was reported that nutrient loading rate explained about 70% and 55% of the annual variation in total nitrogen (TN) and total phosphorus (TP) concentrations, respectively (Conley *et al.*, 2000). Concentrations of both DIN and TN were highest during winter and lowest during summer. The relative uniformity in annual patterns of N and P concentration in Danish estuaries is consistent with the similarity in their structure, with most being small and shallow, with relatively short water residence times and heavily loaded with agricultural N and P. A large estuarine characterization was completed by Bricker *et al.* (1999) in which 143 estuaries, representing about 90% of USA estuarine surface area, was examined for symptoms of eutrophication. Nitrogen was identified as a major cause of eutrophication, but this effort stopped short of examining data for patterns of N distribution.

Twenty years ago issues concerning dissolved organic nitrogen (DON) were just emerging onto research agendas, measurement techniques were in early stages of development, little was known concerning the various compounds comprising the DON pool, sources and sinks were not well established, and there were only a limited number of measurements available. Much has changed concerning all of these issues, resulting in the development of several important reviews, one from just over a decade ago (Antia *et al.*, 1991) and two more recent works (Berman and Bronk, 2003; Bronk, 2002). Additionally, Burdige and Zheng (1998) developed a summary of DON exchanges between water and sediments in coastal and estuarine systems. We have added several more total dissolved nitrogen (TDN) and DON concentration measurements to those provided by Berman and Bronk (2003; Table 18.1). Several important points are clear. In most estuaries DON ranges from an important (30–40%) to the dominant (>80%) component of the dissolved N pool. DON is operationally defined but is actually a complex mixture of N-compounds with widely differing chemistries, sources and sinks. We echo here the conclusions of Berman and Bronk (2003) that DON is not just a conservative N pool, can have strong source and sink pathways in estuaries and needs more explicit consideration in evaluations of the N economy of estuaries.

2.2. Comparative examination of nitrogen distributions

We re-visited the issue of water column N distributions to see if we could find distinctive seasonal patterns related to estuarine type, location within an estuary and climate variability (i.e., wet, dry, average inflow conditions). We obtained ammonium (referred to hereafter as NH_4), nitrite (NO_2), nitrate (NO_3), and phosphate (PO_4) concentration data from 44 USA estuarine systems. Several locations (e.g., tidal freshwater, oligohaline, mesohaline, polyhaline) were selected in some systems and in a dozen cases we also obtained concentration data during dry, average and wet years (Frank *et al.*, 2007).

Annual $NO_2 + NO_3$ concentrations in surface waters of 44 estuarine sites ranged from 0.05 to 150 μM (Fig. 18.1). Highest concentrations tended to occur in river dominated estuaries and lowest in dry and sub-tropical systems. As expected, concentrations were highest in tidal freshwater or oligohaline locations and decreased seaward. Despite the fact that all data in Fig. 18.1 were collected during average inflow years the range in concentrations was large. This is likely a reflection of the multiple factors, including N input rates, water residence times, and biological uptake, which influence concentrations. In a smaller set of estuaries, $NO_2 + NO_3$ concentrations were available for dry, average and wet years (Fig. 18.2). In Chesapeake Bay there were large differences in concentration between dry and wet years in the polyhaline and mesohaline sites; $NO_2 + NO_3$ was always high in the oligohaline zone because of proximity to the riverine N-source and limited uptake by phytoplanlton in this turbid portion of the system. Systems as different from Chesapeake Bay as Florida and Tomales Bays exhibited similiar but muted patterns. Differences between wet and dry year $NO_2 + NO_3$ concentration were very small or reversed in four of these systems indicating that generalities, even concerning such a common compound as $NO_2 + NO_3$, are hard to find.

Strong seasonal patterns were evident for $NO_2 + NO_3$ and PO_4 concentrations (Fig. 18.3). Nitrite + nitrate concentrations were highest during winter; if winter and

Table 18.1 Concentrations of Total Dissolved Nitrogen (TDN) and Dissolved Organic Nitrogen (DON) from Surface Waters of a Variety of Estuarine Systems

Location	TDN (μM N)	DON (μM N)	% DON	Method	Source
Shinnecock Bay, NY	2–4.9	0.6–4	30–88	PO	Berman and Bronk, 2003
Waquoit Bay, MA	140	40	29	NG	Berman and Bronk, 2003
Chesapeake Bay, mesohaline	34	21	62	PO	Berman and Bronk, 2003
Chesapeake Bay, mesohaline	43	22	51	PO	Berman and Bronk, 2003
Chesapeake Bay, mesohaline	23	22	96	PO	Berman and Bronk, 2003
Chesapeake Bay, polyhaline		16		UV	Berman and Bronk, 2003
Patuxent River, tidal fresh	70	29	41	PO	This study
Patuxent River, oligohaline	76	27	36	PO	This study
Patuxent River, mesohaline	33	24	73	PO	This study
Maryland Cstl. Bay, oligohaline	63	45	72	PO	This study
Maryland Cstl. Bay, polyhaline	40	37	93	PO	This study
Apalachicola Bay, FL	23	15	65	PO	Berman and Bronk, 2003
Delaware estuary		41		PO	Berman and Bronk, 2003
Elbe estuary	72	65	90	PO	Berman and Bronk, 2003
North Inlet, SC	19–35	18–31	87–93	NG	Berman and Bronk, 2003
Tomales Bay, CA		6–13		UV	Berman and Bronk, 2003

Source: Berman and Bronk (2003).
Entries labeled "this study" are from the Chesapeake Bay Water Quality Monitoring Program (2004). Measurement methods included: PO, persulfate oxidation; UV, ultraviolet oxidation; NG, not given.

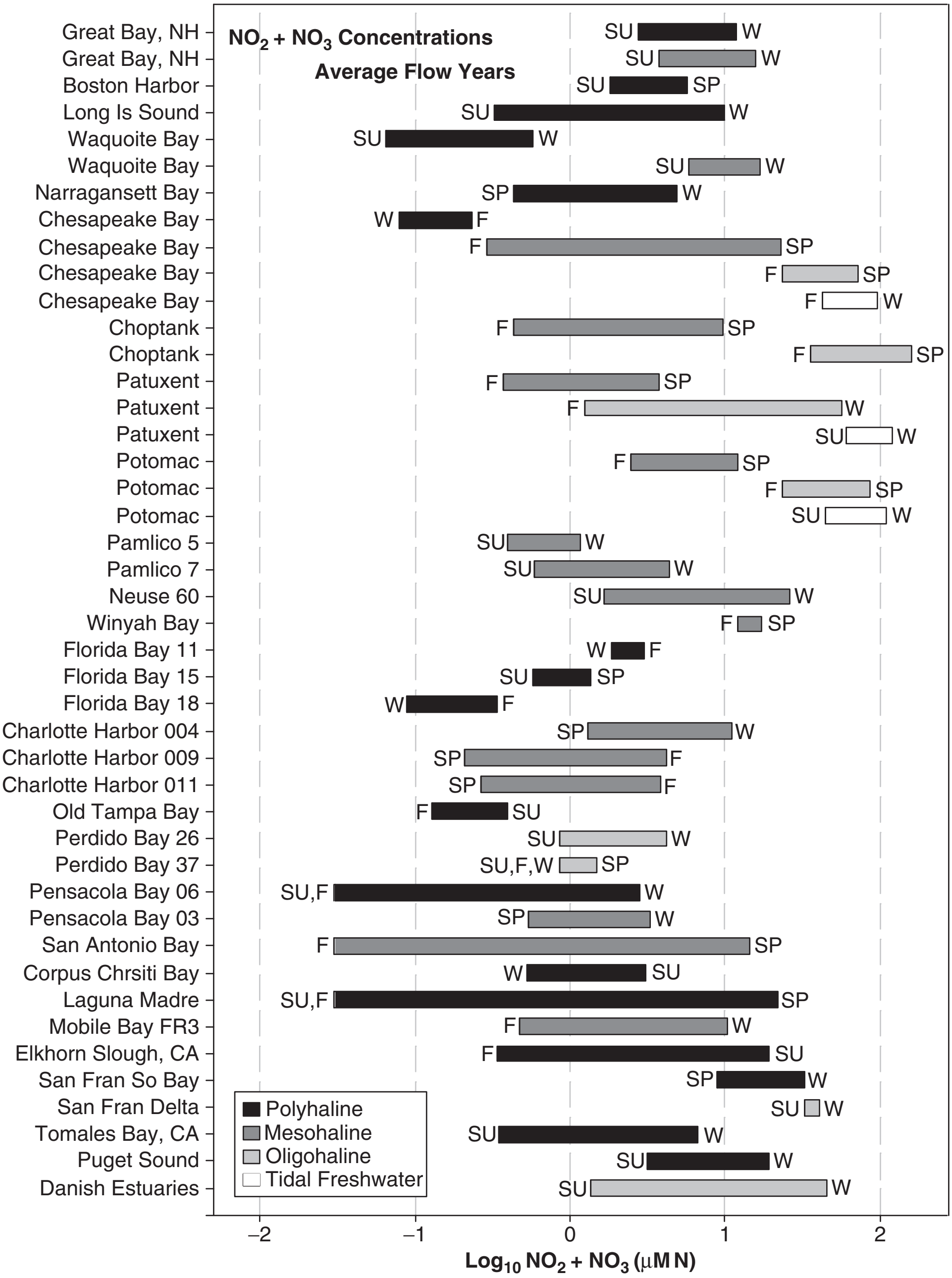

Figure 18.1 Bar graph of maximum and minimum $NO_2 + NO_3$ concentrations measured in a variety of USA estuaries during years of average freshwater inflow conditions. Location of samples from these systems is indicated by salinity regime (tidal freshwater, TF; oligohaline, O; mesohaline, M and polyhaline, P). Season in which maximum and minimum concentrations occurred are also indicated (winter, W; spring, Sp; summer, Su; fall, F). Data were compiled by Frank *et al.* (2007).

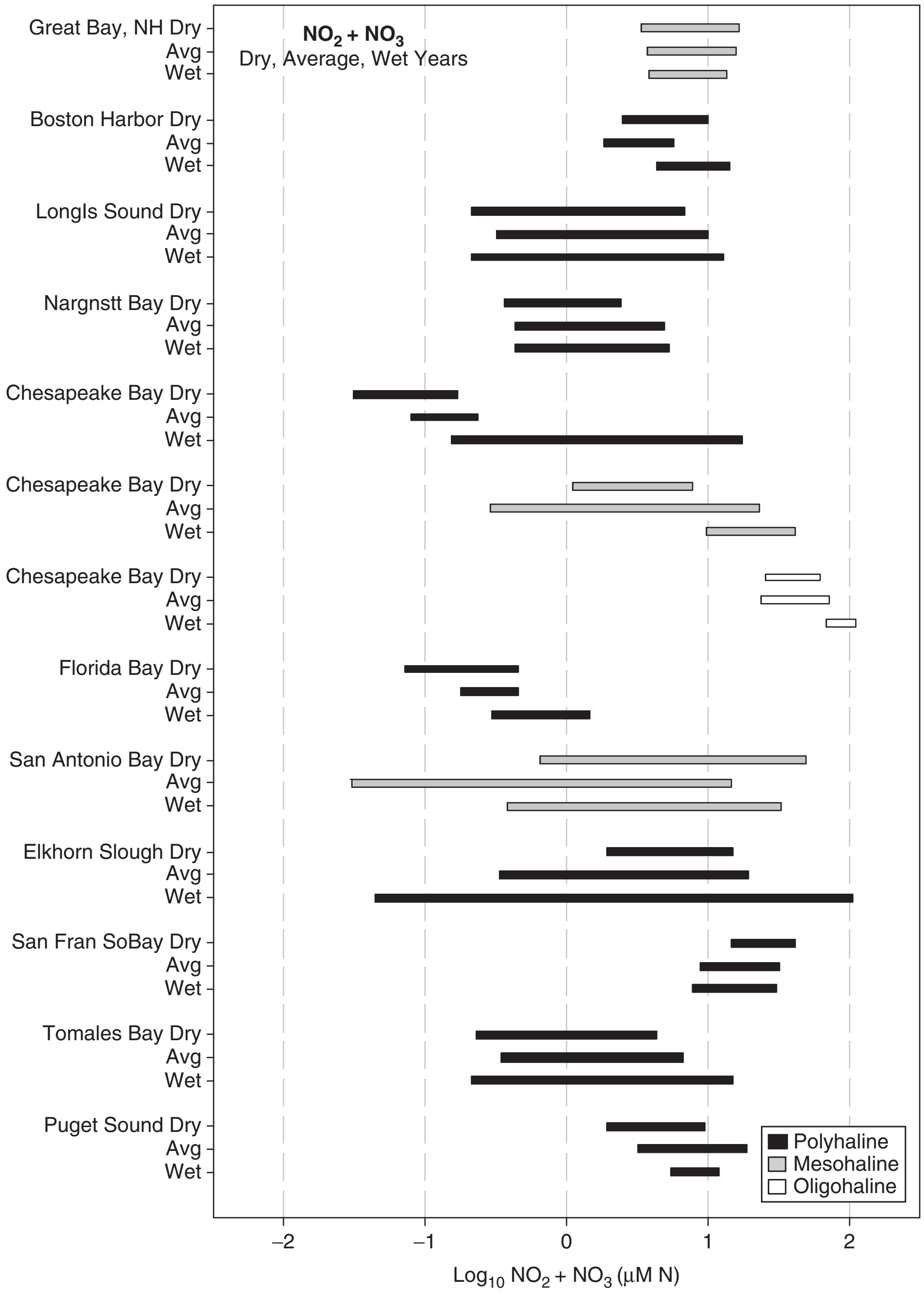

Figure 18.2 Summary of maximum and minimum $NO_2 + NO_3$ concentrations measured in a selection of USA estuaries during wet, average and dry years. Location of samples from these systems is indicated by salinity regime (tidal freshwater, TF; oligohaline, O; mesohaline, M and polyhaline, P). Season in which maximum and minimum concentrations occurred are also indicated (winter, W; spring, Sp; summer, Su; fall, F). Data were compiled by Frank *et al.* (2007).

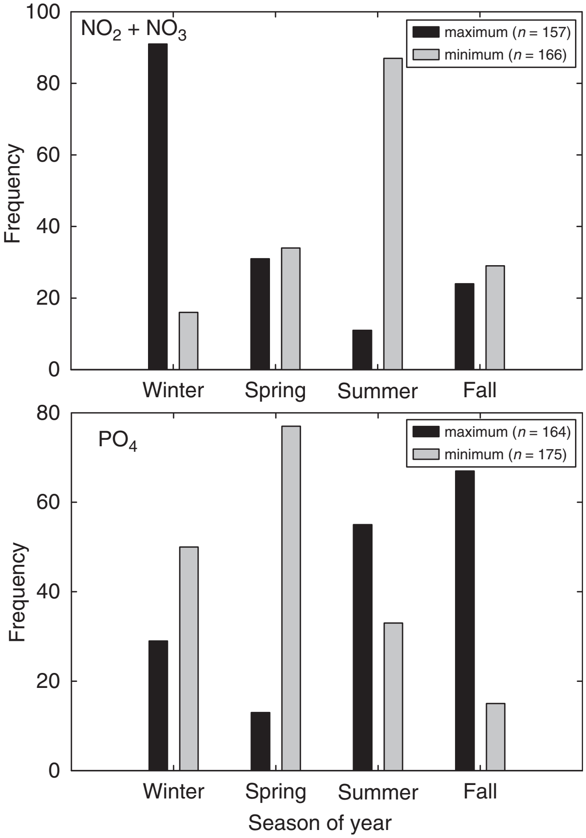

Figure 18.3 Frequency distribution of season in which maximum and minimum $NO_2 + NO_3$ and PO_4 concentrations were observed in a variety of USA estuarine systems. Data were compiled by Frank *et al.* (2007).

spring frequencies of maximum concentration are combined, then 80% of all maximum concentrations occurred during these seasons. Seasonal minimum concentrations mainly occurred during summer. Seasonal maximum PO_4 concentrations generally occurred during summer or fall, opposite the pattern observed for $NO_2 + NO_3$. Seasonal minimum concentrations of PO_4 were most frequently observed during spring, the time of the year that P has been found to limit spring diatom blooms (e.g., Fisher *et al.*, 1999). DIN: DIP ratios were also computed and grouped by categories as a frequency histogram (Fig. 18.4). The most frequently encountered category was less than 10:1 (40%) which suggests potential N-limitation, and almost 60% of all ratios were less than 20:1. The seasonal differences in N (high in winter-spring) and P (high in summer-fall) concentrations certainly play into creating this distribution of ratios. Given that nutrient inputs to many estuarine ecosystems are rich to very rich in DIN relative to DIP, net biogeochemical processes tend to reduce dissolved N concentrations relative to dissolved P concentrations.

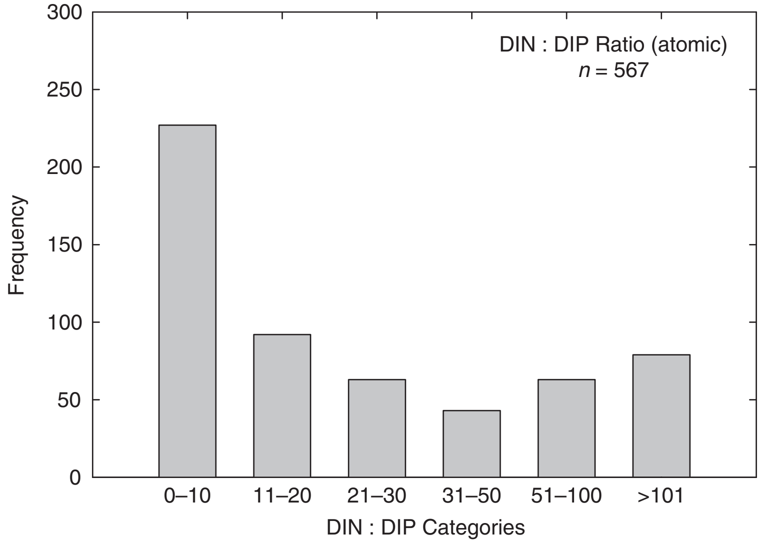

Figure 18.4 Frequency distribution of DIN:DIP ratios computed for a variety of USA estuarine systems. Data were compiled by Frank *et al.* (2007).

2.3. Detailed distributions in Chesapeake bay

While the analyses presented above suggest a wide range of variability in N distributions among estuarine systems, here we examine temporal and spatial patterns for one well-studied estuarine system. An intensive monitoring program in Chesapeake Bay and its tributaries during the past twenty years has experienced a wide range of hydraulic conditions. We summarized N distribution data to illustrate effects of season, location, depth and hydrology.

Monthly surface water nitrate concentrations in three salinity regions (oligohaline, mesohaline and polyhaline) in Chesapeake Bay are displayed as box and whisker plots and as mean values for wet or dry (i.e., high or low river flow) conditions (Fig. 18.5). Strong seasonal patterns are evident throughout the system for wet years and for dry years in all but the polyhaline. Differences between NO_3 concentrations in wet and dry years were pronounced in winter and spring but disappeared during fall. Differences in NO_3 concentrations with river flow in the mesohaline region were similar to the range in algal biomass observed between wet and dry years (Boynton and Kemp, 2000). Peak concentrations occurred in the polyhaline region only a month after the seasonal peaks occurring 300 km farther up the Bay. Harding and Perry (1997) reported the largest changes in algal biomass in the polyhaline zone during a 50 year period of increased nutrient loading, consistent with the NO_3 distribution pattern found between wet and dry years.

Whereas higher nitrate concentrations in surface (compared to bottom) waters reflect NO_3 sources in watershed runoff, higher concentrations of NH_4 in bottom waters derive from recycling processes occurring in the aphotic sediments (Fig. 18.6; Kemp and Boynton, 1992). Seasonal variations in bottom water NH_4

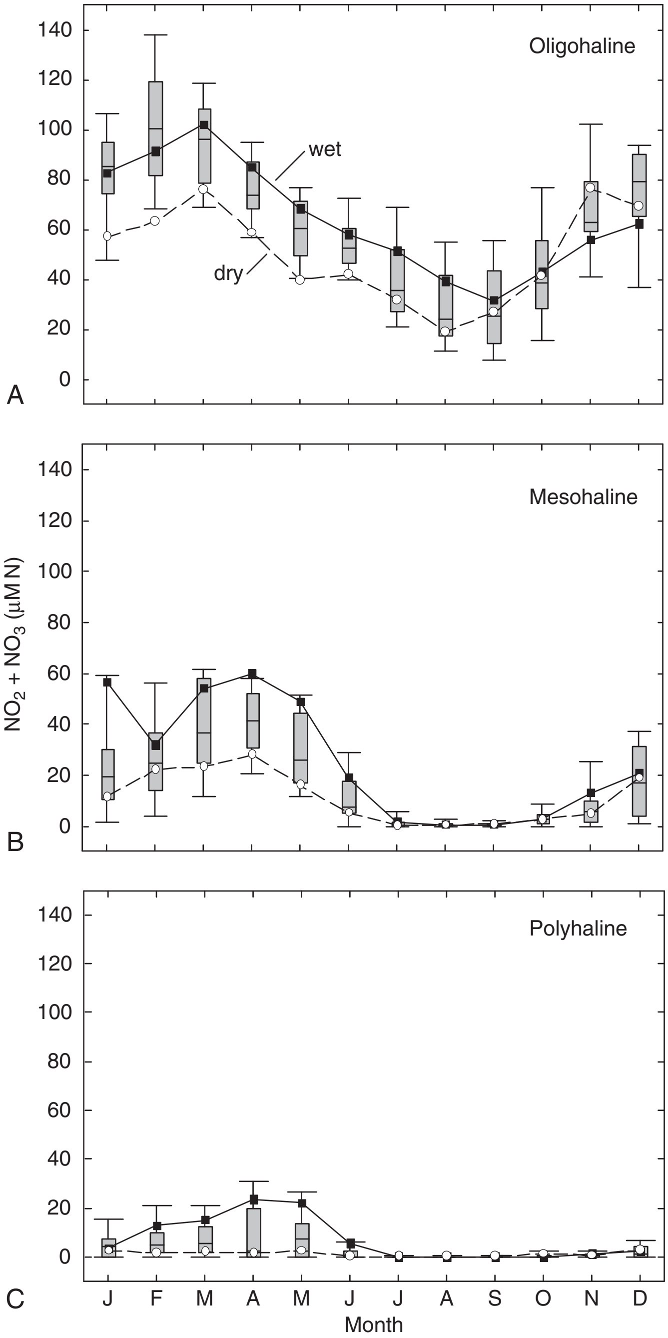

Figure 18.5 Surface water $NO_2 + NO_3$ concentrations measured at stations located in the oligohaline (A), mesohaline (B), and polyhaline (C) regions of Chesapeake Bay. The box and whisker plots contain all values for each month in the 20 year data set (1985–2004). Dark squares and circles represent $NO_2 + NO_3$ concentrations during all wet and dry years, respectively, in this 20 year data set. Data were from the Chesapeake Bay Water Quality Monitoring Program (2004).

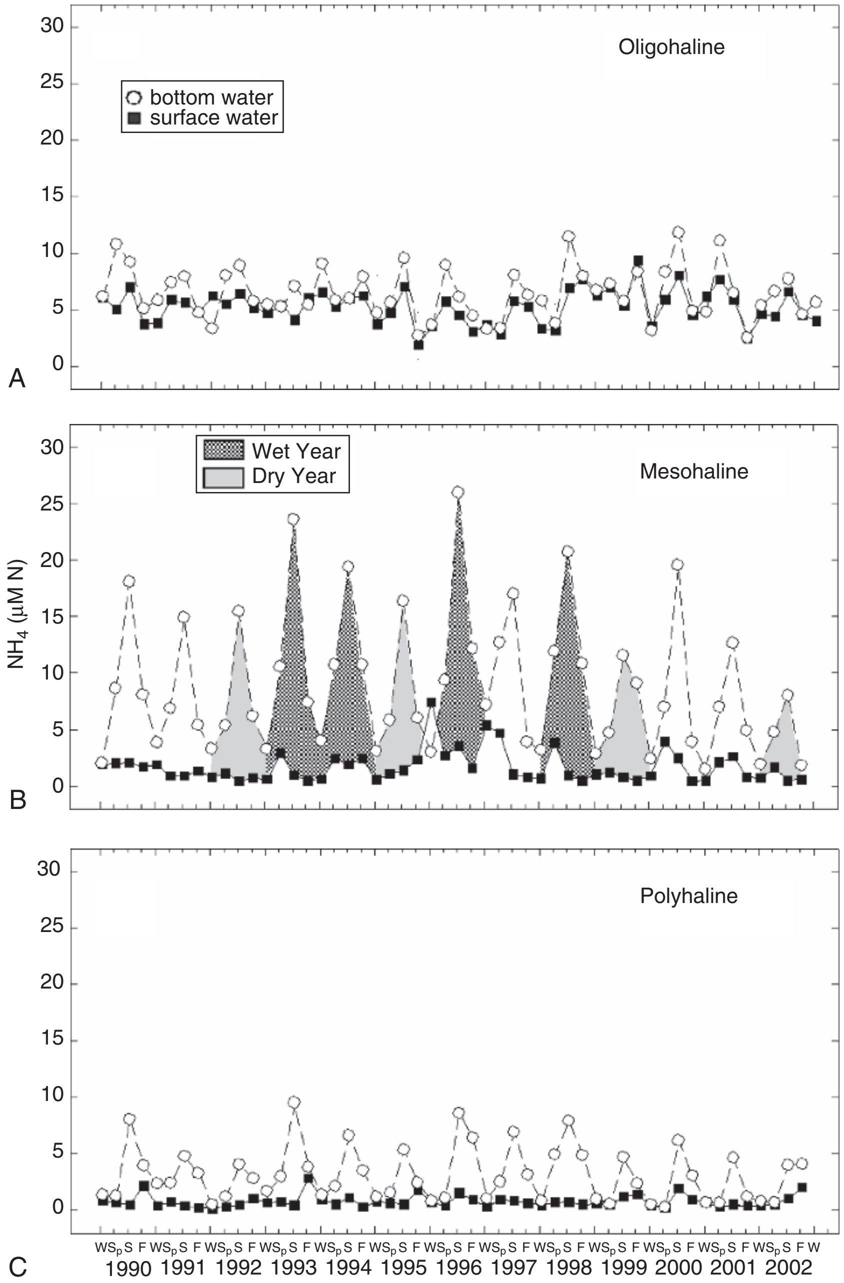

Figure 18.6 Surface and bottom water NH$_4$ concentrations measured at stations located in the oligohaline (A), mesohaline (B), and polyhaline (C) regions of Chesapeake Bay. Monthly or bi-monthly data in the 20 year data set (1985–2004) were averaged to seasons. Data were from the Chesapeake Bay Water Quality Monitoring Program (2004).

concentrations were most pronounced in the stratified portions of Chesapeake Bay, particularly in the mesohaline and polyhaline area, where deposited phytoplankton blooms provided labile substrate for decomposition processes. Seasonal patterns and vertical differences in NH_4 were not as evident in the oligohaline portion of the Bay, probably because of stronger vertical mixing and less deposition of labile phytodetritus. During years of very high river discharge, summer peak NH_4 concentrations in bottom waters of the mesohaline, and even the polyhaline Bay, clearly reflected these flow conditions.

Finally, we examined the seasonal distribution of NO_3 along the salinity gradient of the Patuxent River estuary, a tributary of Chesapeake Bay (Fig. 18.7). While these ''mixing diagrams'' have inherent interpretive limitations (e.g., Nixon and Pilson, 1983), these plots of nitrate concentration versus salinity provide a format to examine variations in non-conservative processing of NO_3 with seasons and hydrologic conditions. The most consistent feature of these data is the very rapid disappearance of NO_3 in low salinity regions during summer under all flow conditions. In contrast, the non-conservative sink behavior of nitrate clearly evident in summer is barely apparent during winter. In addition, concentrations in the tidal freshwater estuarine zone tend to be higher and lower during dry and wet winters, respectively, suggestive of solute dilution with increasing river flow. These seasonally modulated patterns of NO_3 loss in excess of dilution are not as evident for NH_4 or PO_4, both of which exhibited more spatial variability and strong indications of internal sources, probably related to intense remineralization in the sub-pycnoline water column and bottom sediments (e.g., Kemp and Boynton, 1984).

3. NITROGEN BUDGETS OF ESTUARINE SYSTEMS

Although many data have been collected and reported concerning N in estuaries only a limited portion has been used to support development of quantitative N-budgets, at the scale of whole ecosystems. Given the early interest in quantifying the sources and fate of N (e.g., Johnstone, 1908), there have been surprisingly few published quantitative estuarine N-budgets. Most of these report rates of N inputs, internal losses and downstream exports for whole estuaries at annual time scales. Nixon *et al.* (1996) have organized annual-scale nutrient budgets for nine estuarine ecosystems.

3.1. Inputs of nitrogen to estuaries

Both the scope and detail of information currently available concerning N inputs to coastal and estuarine waters has changed dramatically since the early work of Meybeck (1982) who reported strong correlations between N concentrations and features of drainage basins (e.g., population density) for 30 rivers. During the late 1980s NOAA organized nutrient load estimates for many estuaries in the USA (e.g., Bricker *et al.*, 1999). More recently, Smith *et al.* (2003) updated the global-scale analysis of Meybeck (1982) using data from 165 rivers to demonstrate that: (1) N and

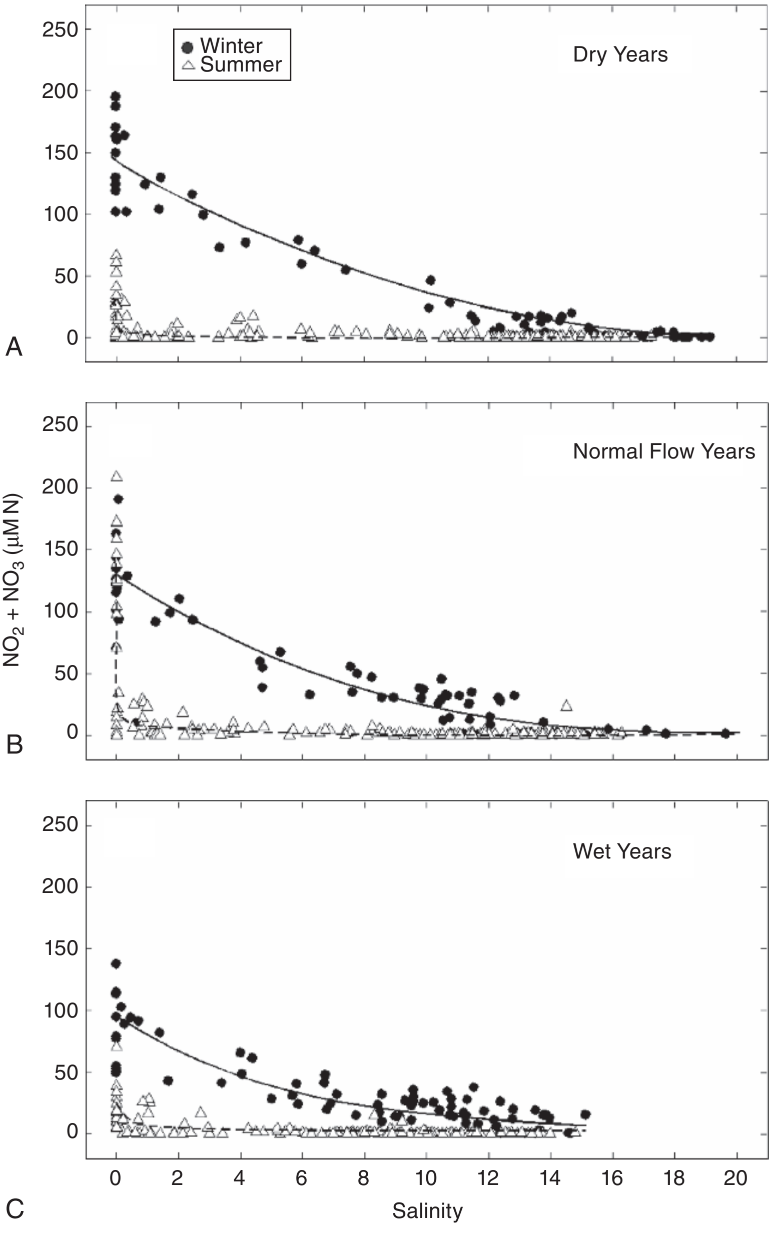

Figure 18.7 Salinity versus concentration plots for $NO_2 + NO_3$ during dry, average and wet years in the Patuxent River estuary. Summer and winter values are shown in each panel. Data were from the Chesapeake Bay Water Quality Monitoring Program (2004).

P loads were statistically related to population density and runoff per unit land area, (2) N and P loads were closely correlated to each other despite different biogeochemistries, (3) loads to coastal waters had increased by a factor of about three since the 1970s. Estimates of future loads to estuaries and the coastal ocean suggest another doubling by 2050 (e.g., Kroeze and Seitzinger, 1998; Chapter 18 by Seitzinger and Harrison, this volume).

Detailed assessments have been reported for anthropogenic N loads to specific river basins and associated riverine N export to adjacent estuaries and coastal waters. Nitrogen exports from a diverse sampling of coastal landscapes appear to be on the order of 20–25% of anthropogenic inputs (Boyer *et al.*, 2002; Castro *et al.*, 2003; Howarth *et al.*, 2002; Van Breemen *et al.*, 2002). A variety of nutrient load models and techniques have also been developed, ranging from those having complex mechanistic structures and goals of high spatial and temporal resolution (Costanza *et al.*, 2002) to simpler, more tractable models designed for use in particular landscapes (e.g., Carmichael *et al.*, 2004; Jordan *et al.*, 2003; Valiela *et al.*, 1997) to very ambitious statistical models used at continental scales (e.g., Smith *et al.*, 1997).

Several recent analyses of nitrogen loads to estuarine systems have been based on direct measurements of loads from riverine and point sources (possible ocean inputs not considered). For example, Conley *et al.* (2000) reported N-loading rates to 81 Danish estuaries for a 7 year period, Nedwell *et al.* (2002) reported DIN loads to 93 mainland United Kingdom estuaries and Carmichael *et al.* (2004) estimated N loads to 15 small Cape Cod estuaries. In addition, estimates of historical N loads suggest 5-fold or larger increases during the last three centuries for both Narragansett Bay (Nixon, 1997) and Chesapeake Bay (Boynton *et al.*, 1995). Recent estimates for Chesapeake (Hagy *et al.*, 2004) and Waquoit Bay (Bowen and Valiela, 2001) suggest more than a doubling of N loads during the previous half-century. Nixon (2003) estimated Nile River nutrient loads to the adjacent Mediterranean sea coast before and after construction of the Aswan High Dam and argued that the loss of nutrients inputs due to damming of the Nile in the 1960s has largely been replaced by anthropogenic inputs associated with run-off of agricultural fertilizers and sewage discharges. Finally, in many estuaries, the adjacent land and atmosphere are the main sources of N, but the adjacent ocean can serve as the main external source of N in some situations. For example, Kelly (1998) estimated that transport of N from the ocean into Boston Harbor provided about twice as much N as land-derived sources. Bricker *et al.* (1999) noted, but did not quantify, ocean derived N as a major nutrient source along the USA Maine coast during portions of the year.

It appears that estuaries are among the most heavily fertilized systems on the planet. To examine the distribution of N-loading rates among well-studied estuaries, we organized a frequency histogram of N loads (on an estuarine area basis and including only loads from landside, but not oceanic, sources) for 218 estuarine systems (Fig. 18.8). The distribution that emerged indicated that most N-loading rates fell within the range of 6–50 g N m^{-2} $year^{-1}$, and only about 15% of the systems had loading rates below 5 g N m^{-2} $year^{-1}$. It is interesting to note that anthropogenic N dosing to major watersheds of the USA ranged from 0.5 to 3.5 g N m^{-2} $year^{-1}$ (Jordan and Weller, 1996) and from 0.9 to about 6 g N m^{-2} $year^{-1}$ for smaller watersheds of USA coastal areas (Castro *et al.*, 2003; Van Breemen *et al.*,

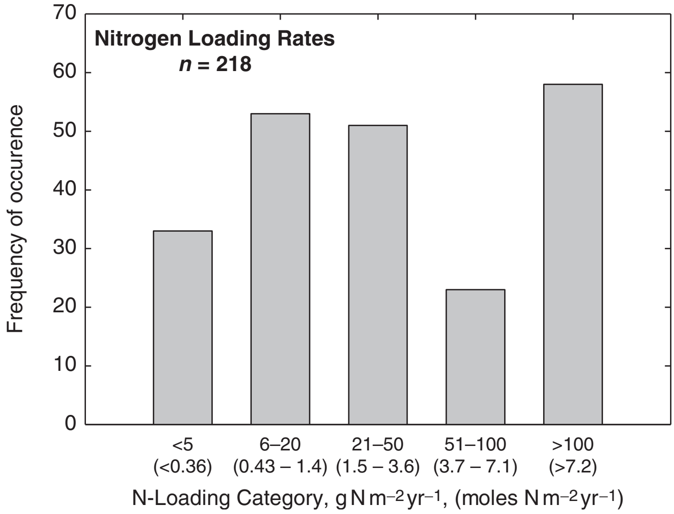

Figure 18.8 Frequency distribution of N-loading rates to a variety of estuarine and coastal marine ecosystems. Data were compiled from Boynton *et al.* (1995), Carmichael *et al.* (2004), Conley *et al.* (2000), Nedwell *et al.* (2002), and Nixon *et al.* (1996).

2002). The anthropogenic rates of N-loading to adjacent estuarine systems are clearly much higher; 37% of the sample exceeded 50 g N m^{-2} year^{-1}, almost an order of magnitude greater than most adjacent land areas.

We also assembled data for 34 estuaries where inputs of both TN and TP (g N or P m^{-2} year^{-1}) were available (Fig. 18.9). There is a very large range in N and P inputs among these estuaries. N loads varied by a factor of almost 200 and P by just over 300; the majority of systems in this sample had N and P loading rates ranging from 5 to 50 and 1 to 10, respectively. Despite the different biogeochemistry of N and P, there was an obvious correlation between loading rates of these elements (Smith *et al.*, 2003). Loading rates for a few systems (e.g., Himmerfjarden, Back River) had especially high N: P ratios because sewage was a major nutrient source and P, but not N, was removed at treatment facilities. In others, elevated N: P ratios were the result of diffuse source inputs that were naturally more enriched in N (mainly NO_3) than P. Finally, it is important to note that loading rates alone are not generally sufficient to predict the trophic status (*sensu* Nixon, 1995) of an estuary. For example, both the Potomac River estuary and Narragansett Bay had similar annual N-loading rates but the Potomac exhibited severe eutrophication characteristics while these were far less severe in Narragansett Bay. Several authors have noted that estuarine morphology, water residence times, water column mixing rates, light conditions and biological communities all have potentially strong influences on the impact of loading rates (e.g., Boynton *et al.*, 1996; Valiela *et al.*, 2000; Wulff *et al.*, 1990). A 25 year record of annual TN and TP loads to Chesapeake Bay from the Susquehanna River was added as an inset to Fig. 18.9 to serve as a reminder that inputs to some estuaries exhibit considerable inter-annual variability. In this

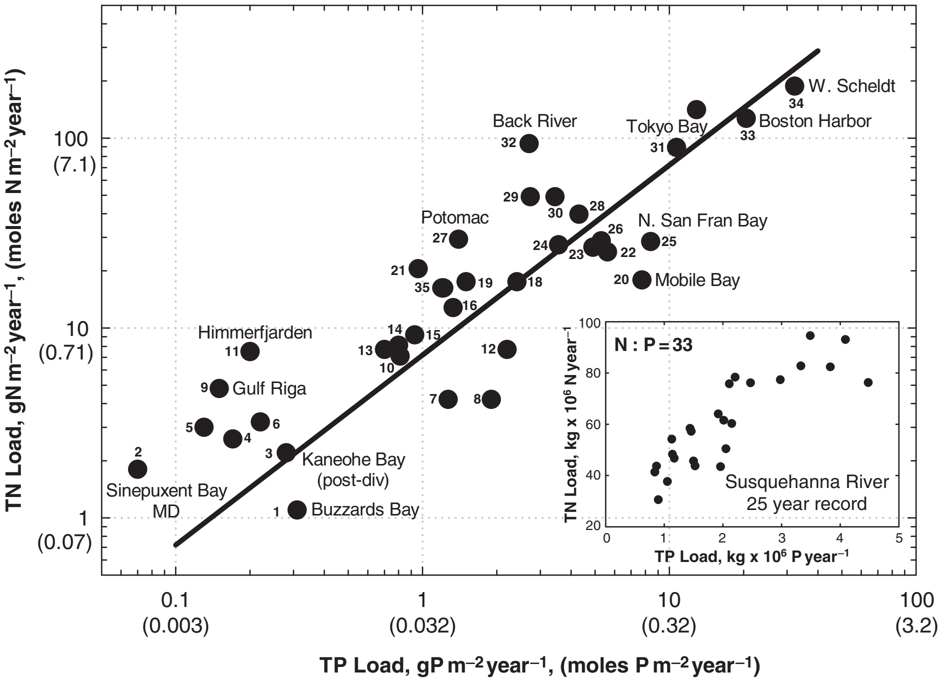

Figure 18.9 A scatter plot of annual TN versus TP loading rates to a selection of coastal, estuarine and lagoon ecosystems. Figure was re-drawn and expanded from Boynton *et al.* (1995). Systems are coded by number: 1 – Buzzards Bay, MA (NOAA/EPA, 1989); 2 – Sinepuxent Bay, MD (Boynton *et al.*, 1992, 1996); 3 – Kaneohe Bay, HI (post-diversion, Smith, 1981); 4 – Isle of Wight Bay, MD (Boynton *et al.*, 1992, 1996); 5 – Baltic Sea (Nixon *et al.*, 1996); 6 – Chincoteague Bay, MD (Boynton *et al.*, 1992, 1996); 7 – Kaneohe Bay, HI (pre-diversion, Smith, 1981); 8 – Narragansett Bay RI (prehistoric; Nixon, 1997); 9 – Gulf of Riga (Yurkovskis *et al.*, 1993); 10 – Albemarle Sound, NC (Nixon *et al.*, 1986); 11 – Himmerfjarden, Sweden (Engqvist, 1996); 12 – Guadaloupe Bay, TX (dry year, Nixon *et al.*, 1996); 13 – Buttermilk Bay, MA (Valiela and Costa, 1988); 14 – Moreton Bay, Australia (Eyre and McKee, 2002); 15 – Seto Inland Sea (Nixon *et al.*, 1986); 16 – Taylorville Creek, MD (Boynton *et al.*, 1992, 1996); 18 – Newport Bay, MD (Boynton *et al.*, 1992, 1996); 19 – N. Adriatic Sea (Degobbis and Gilmartin, 1990); 20 – Mobile Bay, AL (NOAA/EPA, 1989); 21 – Chesapeake Bay, MD (Boynton *et al.*, 1995); 22 – MERL (1x), RI (Nixon *et al.*, 1986); 23 – Delaware Bay, DE (Nixon *et al.*, 1996); 24 – Narragansett Bay, RI (current, Nixon *et al.*, 1996); 25 – N. San Francisco Bay, CA (Hager and Schemel, 1992); 26 – Guadaloupe Bay, TX (wet year, Nixon *et al.*, 1996); 27 – Potomac River estuary, MD (Boynton *et al.*, 1995); 28 – St Martins River, MD (Boynton *et al.*, 1992, 1996); 29 – Apalachicola Bay, FL (NOAA/EPA, 1989; Mortazavi *et al.*, 2000); 30 – Patapsco River Estuary, MD (Stammerjohn *et al.*, 1991); 31 – Tokyo Bay, Japan (Nixon *et al.*, 1986); 32 – Back River, MD (Boynton *et al.*, 1998); 33 – Boston Harbor, MA (pre-sewage diversion, Nixon *et al.*, 1996); 34 – Western Scheldt, Netherlands (Nixon *et al.*, 1996). The solid diagonal line represents the Redfield ratio of TN:TP inputs (weight basis). The inset shows the same variables from a 25 year time series of loading to Chesapeake Bay from the Susquehanna River. The N:P load ratio in the inset is weight based (Chesapeake Bay Water Quality Monitoring Program, 2004).

example, TN and TP loads varied by factors of about 3 and 5, respectively, and were very rich in N relative to P (TN:TP = 33 by weight). There was a strong indication that the TN:TP load ratio decreased during high load years, probably because more sediment, and sediment-bound P, were eroded and transported during wetter than average conditions. Thus, both the quantity and composition of nutrient inputs can vary by substantial amounts due to climate variability.

In general, variations in N-loading rates are reflected in concentrations of N in receiving water bodies. Although many processes act to modify nutrient concentrations at various rates, mean TN concentrations were significantly correlated to TN loading for five sub-systems of Chesapeake Bay averaged over a decadal period and for interannual variations in annual mean values for the Potomac River estuary (Fig. 18.10; Boynton and Kemp, 2000). Conley *et al.* (2000) reported that on an annual basis about 70% on the variation in TN concentration could be explained by variation in TN loads in a large sample of Danish estuaries.

A review of nitrogen sources to estuaries would not be complete without some discussion of nitrogen fixation, an internal source of nitrogen. A comprehensive review of nitrogen fixation in the world oceans is provided by Carpenter and Capone (Section IIIA, this book). Understanding of the magnitude, factors controlling dinitrogen (N_2) fixation rates and the ecological significance of this process in estuarine ecosystems has received considerable attention in the last few decades.

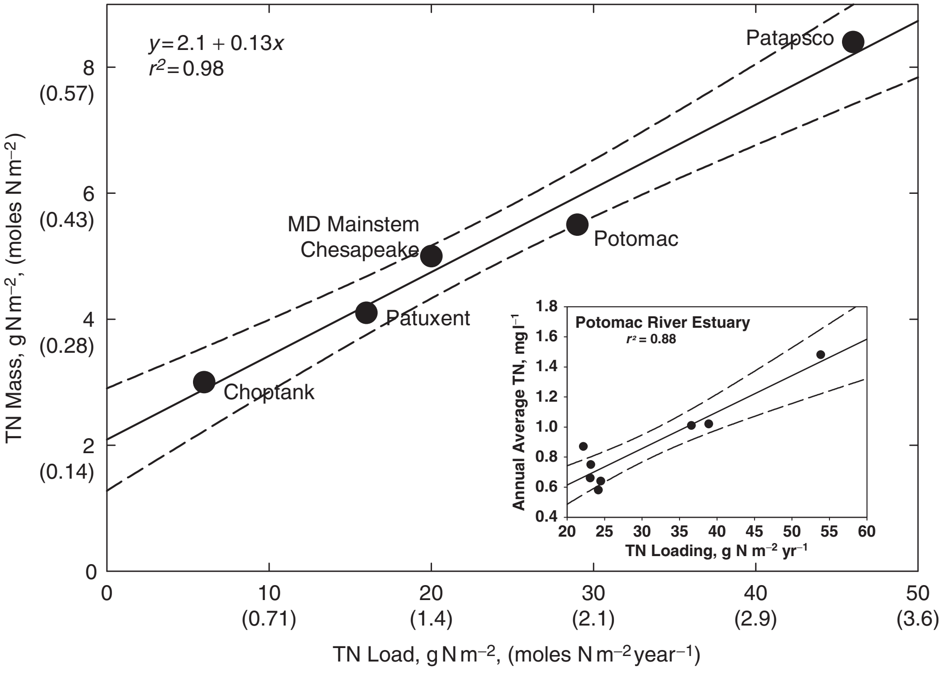

Figure 18.10 Scatter plot of average annual TN mass versus average annual TN loads for a portion of Chesapeake Bay and a selection of Chesapeake Bay tributary rivers. All concentration data were from sampling stations located in the mesohaline regions of the Bay and tributary rivers. Inset shows annual TN concentrations versus TN loads to the Potomac River estuary for an 8 year period. All data were from the Chesapeake Bay Water Quality Monitoring Program (2004).

It appears that in aphotic sediments and in estuarine water columns, N_2 fixation rates tend to be low and not of ecological significance at the level of whole estuarine systems (e.g., Affourtit *et al.*, 2001; Burns *et al.*, 2002; Howarth *et al.*, 1988a, Marino *et al.*, 2002; Paerl *et al.*, 1987). However, in photic sediments of coral reefs (Capone *et al.*, 1992; Koop *et al.*, 2001), salt marshes (Nielsen *et al.*, 2001) and seagrass communities (McGlathery *et al.*, 1998; Welsh, 2000) N_2 fixation rates tend to be higher and of importance to the nitrogen economy of these localized communities (see also Carpenter and Capone, this volume, O'Neil and Capone, this volume; Hopkinson and Giblin, this volume; McGlathery, this volume).

Howarth *et al.* (1988a) reported N_2 fixation rates to be low (<0.2 g N m^{-2} $year^{-1}$) in bare estuarine sediments, higher in organic-rich estuarine sediments (0.4–1.6 g N m^{-2} $year^{-1}$) and higher still in cyanobacterial mats (1–76 g N m^{-2} $year^{-1}$). Herbert (1999) and Welsh (2000) developed excellent summaries of estuarine N_2 fixation rates for a variety of sub-systems and reached similar conclusions. In these more recent summaries, bare sediment rates ranged from 0.03 to 0.65 g N m^{-2} $year^{-1}$, rates in cyanobacterial mats associated with salt marshes and reefs ranged from about 1–10 g N m^{-2} $year^{-1}$ in temperate areas and were higher in the tropics and rates in seagrass communities ranged from about 0.1 to 6 g N m^{-2} $year^{-1}$ in temperate areas and from 10 to 40 g N m^{-2} $year^{-1}$ in tropical locations. Comparing these rates to loading rates of N from external sources (Figs. 18.8 and 18.9) indicates that N_2 fixation is not a dominant source of "new nitrogen" to most estuaries, although it can be an important feature in some estuarine communities, especially in oligotrophic tropical systems (Welsh, 2000).

Understanding of the factors controlling N_2 fixation rates in estuarine water columns and sediments is also evolving. Suppression of water column N_2 fixation rates by iron limitation and sulfate inhibition of molybdenum uptake have been found to be important features in oxic environments and less so in reducing environments (Howarth and Cole, 1985; Howarth *et al.*, 1988b). Paerl *et al.* (1987) reported increased N_2 fixation rates with the addition of labile organics and suggested that additional substrate and the associated creation of anoxic microzones enhanced rates. In a recent series of papers Marino *et al.* (2002, 2003, 2006) found low N_2 fixation rates by planktonic estuarine cyanobacteria under nitrogen limited conditions to be caused by a combination of intrinsic slow growth, grazing by estuarine zooplankton and sulfate- molybdenum interactions. Thus, estuarine N_2 fixation rates much lower than those typically observed in nitrogen limited lakes appear to be the result of both top-down and bottom-up effects.

3.2. Internal losses of nitrogen

Compared to N inputs, the internal loss terms of estuarine N-budgets are not as well documented. In general, internal losses include burial of PN in accreting sediment columns and denitrification in either the water column or sediments (see also Devol, this volume). A few nutrient budgets have estimated N-extraction in the harvest of fish and shellfish biomass and fish migration from estuaries.

Estimates of long-term PN burial (Table 18.2) illustrate a substantial range in rates from very small values (0.05–0.2 g N m^{-2} $year^{-1}$) in the deepest systems to

Table 18.2 Summary of Long-Term Particulate Nitrogen (PN) Burial Rates for Several Tidal Marshes and a Selection of Estuarine and Coastal Marine Ecosystems

Ecosystem type	Location	N-burial rate (g N m^{-2} $year^{-1}$)	N-burial rate (mmol N m^{-2} $year^{-1}$)	Reference
Tidal marshes	N. Carolina	1.3–4.1	93–293	Cited in Merrill, 1999
	Louisiana	21	1500	Cited in Merrill, 1999
	N. Carolina	6.9–10	493–714	Cited in Merrill, 1999
	Choptank River	19–27	1367–1929	Cited in Merrill, 1999
	Monie Bay	14	1000	Merrill, 1999
	Patuxent River	21	1500	Merrill, 1999
	Hudson River	2.3–16	164–1143	Merrill, 1999
	Delaware Bay	2.5	179	Cited in Nixon *et al.*, 1996
Estuaries	Chesapeake digohaline	11	786	Boynton *et al.*, 1995
	Chesapeake mesohaline	3.5	250	Boynton *et al.*, 1995
	Patuxent oligohaline	14	1000	Boynton *et al.*, 1995
	Patuxent mesohaline	5	357	Boynton *et al.*, 1995
	Potomac mesohaline	10	714	Boynton *et al.*, 1995
	Choptank mesohaline	1.7	121	Boynton *et al.*, 1995
	Delaware Bay	1.1	79	Cited in Nixon *et al.*, 1996
	Narragansett Bay	3.3	236	Cited in Nixon *et al.*, 1996
	Guadalupe Bay	0.5	36	Cited in Nixon *et al.*, 1996
	Ochlockonee Bay	1.6	114	Cited in Nixon *et al.*, 1996
	Boston harbor	2.6	186	Cited in Nixon *et al.*, 1996
	Scheldt estuary	14	1000	Cited in Nixon *et al.*, 1996
River Deltas	Mississippi-Atchafalaya	5.6	400	Milliman and Syvitski, 1992
	Grijalva-Usumacinta	2.5	179	Milliman and Syvitski, 1992
	Magdelena	58	4143	Milliman and Syvitski, 1992
	Orinoco	4	286	Milliman and Syvitski, 1992

Table 18.2 (*continued*)

Ecosystem type	Location	N-burial rate (g N m^{-2} $year^{-1}$)	N-burial rate (mmol N m^{-2} $year^{-1}$)	Reference
	Amazon	4.6	329	Milliman and Syvitski, 1992
Deeper coastal	Baltic Sea	0.2	14	Larsson *et al.*, 1985
Deeper coastal	Baltic Sea	0.2	14	Larsson *et al.*, 1985
Systems	Laurentian Channel	0.1	7	Muzuka and Hillaire-Marcel, 1999
	Labrador Sea	0.05	4	Muzuka and Hillaire-Marcel, 1999

Methods used to determine PN burial rates varied but all included an estimate of sediment accumulation rate (^{210}Pb, sediment budget, pollen grain analysis) and an estimate of PN concentration at a depth in the sediment column where concentrations were constant with further depth.

very high rates for river deltas and tidal marshes (>20 g N m^{-2} $year^{-1}$). Although the small values in deep systems suggest processing of PN during transit through deep water columns (Hargrave, 1973; Kemp *et al.*, 1992), high variability in rates among systems with similar depths indicates other influences. In a synthesis of nutrient (N and P) budgets for 9 estuarine ecosystems, burial of PN was a prominent term in only two systems (>35% of TN inputs buried) while in the others burial accounted for 12% or much less of TN inputs (see Nixon *et al.*, 1996 for nutrient budget details for 9 estuarine ecosystems). The two systems in which burial was important (Patuxent and Potomac River estuaries) are sediment-rich, eutrophic estuaries, with relatively long water residence time (2–4 months). Of the other systems considered (Nixon *et al.*, 1996), some had high loading rates but short residence times (e.g., Boston Harbor), while others had limited sediment supplies (e.g., Narragansett Bay). We suggest that PN burial can be an important internal loss in some sediment-rich systems, but limited measurements make this conclusion speculative.

Denitrification, which represents a potentially important process for removing fixed N from estuaries, occurs predominantly in the upper stratum of sediments where rates tend to be limited by availability of nitrate. Nitrate is also produced via nitrification near the sediment surface which is, in turn, limited by availability of oxygen. A recent review of denitrification rates in aquatic systems included 1757 measurements from 152 sites over 45 years (Greene, 2005a; Fig. 18.11 insert; see also Chapter 18 by Devol, this volume). Since the 1960s at least nine different techniques were used to measure denitrification. The most frequently used method was the "acetylene block" technique in which acetylene is used to inhibit the reduction of N_2O to N_2, with N_2O accumulation used as a proxy for N_2 production. The acetylene technique was introduced in the 1970s and use peaked in the 1990s. There has been a growing interest in direct measurements of N_2 production since

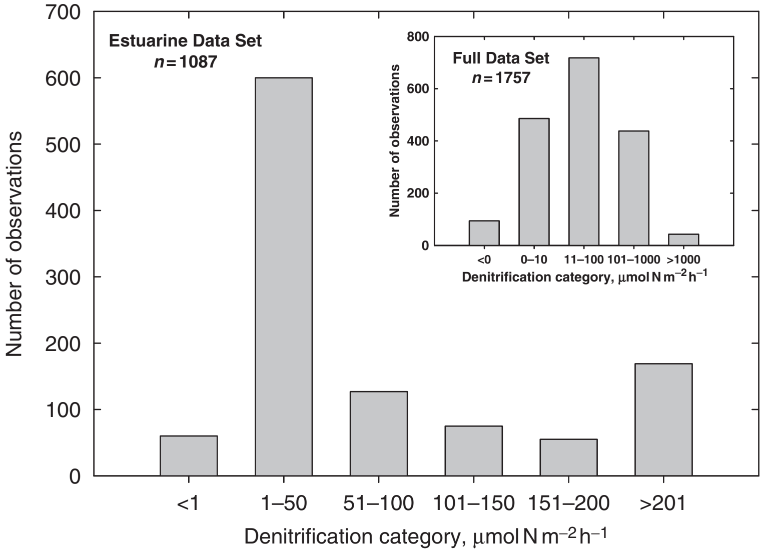

Figure 18.11 Frequency distribution of denitrification measurements from a variety of estuarine ecosystems. The inset is a frequency histogram using denitrification measurements from all aquatic systems. Both figures used data from the denitrification summary developed by Greene (2005a).

the 1980s. In the mid-1990s, isotope pairing and membrane inlet mass spectrometric (MIMS) techniques were developed and the use of the acetylene technique declined substantially.

Most reported denitrification measurements indicated rates between 11 and 100 μmol N m^{-2} h^{-1}, with few rates <1 μmol N m^{-2} h^{-1} and few in excess of 1000 μmol N m^{-2} h^{-1} (Fig. 18.11). In estuarine systems (Fig. 18.11) the most commonly reported rates were between 1 and 50 μmol N m^{-2} h^{-1}, but almost 40% of measurements were larger. Estuaries were also the most intensively measured systems (56% of all measurements), although many estimates were also available for continental shelves, coastal wetlands, lakes, lagoons, inland wetlands and several other environments (Table 18.3). The lower limit of rates in most environments was <1 μmol N m^{-2} h^{-1} while maximum rates ranged from 167 μmol N m^{-2} h^{-1} in seagrass communities to 24,142 μmol N m^{-2} h^{-1} in human engineered systems. Maximum rates above 1000 μmol N m^{-2} h^{-1} were also measured in freshwater creeks, coral reefs, continental shelf and estuarine environments, with maximum estuarine rates reaching nearly 20,000 μmol N m^{-2} h^{-1} in an area near a sewage treatment plant discharge. Mean rates in most systems were between 50 and 250 μmol N m^{-2} h^{-1}. It is useful to note that denitrification rates of 200 μmol N m^{-2} h^{-1} are equal to about 25 g N m^{-2} $year^{-1}$, a substantial fraction of TN loading rates to many estuaries (Fig. 18.8).

Several earlier papers helped place denitrification, as an internal loss term, into the context of the N economy of estuaries. Seitzinger (1988) summarized available

Table 18.3 Summary of denitrification rates from a variety of aquatic ecosystems. These data were from a summary developed by Greene (2005a)

	Denitrification rate, µmol N m^{-2} h^{-1}				
System type	Minimum	Maximum	Mean	Median	Number of measurements
Lakes	0	490	125	100	91
Freshwater creeks	0	1500	266	13	17
Freshwater wetlands	0	330	39	4	52
Human engineered systems	0	24142	1497	8	55
Tidal mudflats	2.1	213	70	30	62
Coastal wetlands	−200	375	96	71	154
Seagrass communities	8.3	167	51	21	7
Coastal lagoons	0	290	19	5	116
Estuaries (sub-tidal)	−93	19616	182	31	1052
Coral reef communities	0	1351	107	19	38
Continental shelf	0	1657	102	13	113

System types are arranged in geographic sequence from land to sea. Total number of measurements = 1757. Negative values indicate that N-fixation rates exceeded denitrification rates.

data from lakes, rivers and estuaries regarding the ecological significance of this process. Important conclusions were that denitrification rates were higher in systems receiving large, anthropogenic nutrient inputs, most of the NO_3 consumed in denitrification apparently came from sediment-based nitrification rather than from the water column and, from a small sampling of estuaries, denitrification rates were proportional to TN loading rates, removing an average of 40% of N inputs. More recently, Nixon *et al.* (1996) computed the proportion of input N removed via denitrification from a larger selection of estuaries and several lakes, with values ranging from 10% to 74%, again indicating the importance of this process.

Although denitrification is an anaerobic process, estuarine rates are often limited by conditions of low bottom water oxygen and organic enrichment of sediments. Resulting low redox conditions, high sulfide concentrations and shallow penetration of oxygen into sediments inhibit nitrification, and consequently denitrification (e.g., Henriksen and Kemp, 1988; Joye and Hollibaugh, 1995; Vanderborght and Billen, 1975). Under these conditions, sediment recycling of N becomes more efficient in that most of the PN deposited to sediments is returned to the water column as NH_4 (Kemp *et al.*, 1990). We identified a limited number of studies in which bottom water dissolved oxygen varied appreciably during the study period and in which denitrification and net sediment-water fluxes of NH_4, NO_2 and NO_3 were also measured. Such data were available from a Danish site (Rysgaard-Petersen *et al.*, 1994) and from several studies conducted in Chesapeake Bay (Kemp *et al.*, 1990 and Cornwell, unpublished data). We developed an index of N recycling efficiency and examined

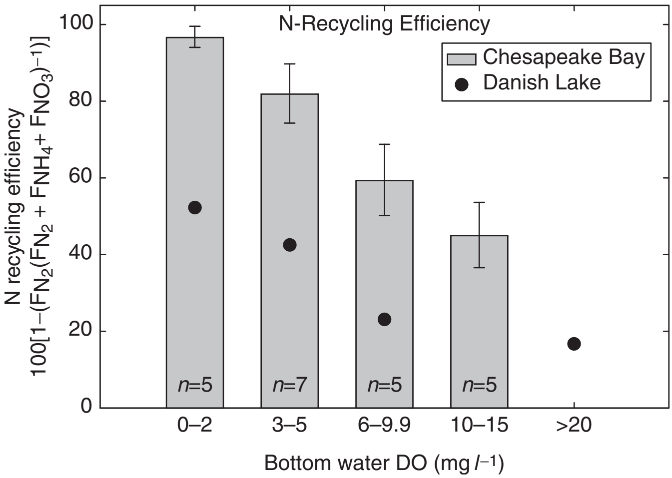

Figure 18.12 Bar graph of N-recycling efficiency as a function of bottom water dissolved oxygen concentration. Bars were based on Chesapeake Bay data reported in Kemp *et al.* (1990) and Cornwell (unpublished data). Solid dots were based on data from Rysgaard-Petersen *et al.* (1994) collected from Vilhelmsborg So, Denmark. Terms in the recycling efficiency calculation (*y*-axis) are: F_{N_2} = flux of N_2 from sediments; F_{NH_4} = flux of ammonium from sediments; F_{NO_3} = flux of nitrate from sediments.

this as a function of bottom water dissolved oxygen concentrations (Fig. 18.12). For both systems there was a consistent increase in cycling efficiency as dissolved oxygen concentrations decrease. This trend suggests that estuarine eutrophication can seriously inhibit N removal via coupled nitrification-denitrification. Clearly, more sites need to be examined to see if this is a general pattern of response. However, the increase in N cycling efficiency with low dissolved oxygen conditions is consistent with the relatively low percent N removal via denitrification in Chesapeake Bay and adjacent tributary rivers, all of which have hypoxic or anoxic bottom waters for portions of each year (Boynton *et al.*, 1995; Hagy *et al.*, 2004).

3.3. Export of nitrogen to downstream systems

The final term in typical nutrient budgets is the export or import of materials to or from the adjacent downstream system. While we have indicated that there has been significant progress in understanding N in estuarine systems, there are also areas with pressing needs for improvement. Export of materials at the mouths of estuaries is a case in point. In most N-budgets the export term was estimated by subtracting the summation of internal losses from the full suite of inputs. The main reason for this non-independent approach was simply because more direct estimates of net flux were too difficult to accomplish. The basic problem is that water fluxes at the mouths of estuaries are relatively large, circulation patterns are often complex (e.g., Boicourt, 1983; Chao *et al.*, 1996; Kjerfve and Proehl, 1979) and the differences in nutrient concentrations across this boundary are often small and variable. Thus, it is extremely difficult to develop accurate estimates of net exchange. It appears that this term will remain uncertain until dependable hydrodynamic models become even more widely available and accessible to those interested in nutrient dynamics.

Despite this difficulty, a recent synthesis of nutrient exchanges between estuaries and coastal waters provides some insights (Nixon *et al.*, 1996). Exports of N from 10 estuarine systems and several lakes ranged from 10% to about 90% of inputs and, as suggested earlier (Boynton *et al.*, 1995), N exports were not well correlated with inputs. The percent of N inputs exported to the coastal ocean was inversely correlated with the log mean residence time of water in the system (Nixon *et al.*, 1996), as has been found for lakes (Kirchner and Dillon, 1975). Adding data for four Chesapeake Bay tributaries to this relationship suggests that other factors (e.g., depth, salinity, nutrient levels) also affect relative export of N (Fig. 18.13). However, despite the widely varying environmental character among these systems, water residence time exerts strong control on the ratio of export to loading. If estuarine communities have sufficient time to process nitrogen, they will, in effect, reduce the N exported via N burial or denitrification. Thus it appears that estuaries can act as either ''pipes'' where N transport rather than transformation is the dominant process or as ''sinks'' for N, all as a function of how long water remains in the system.

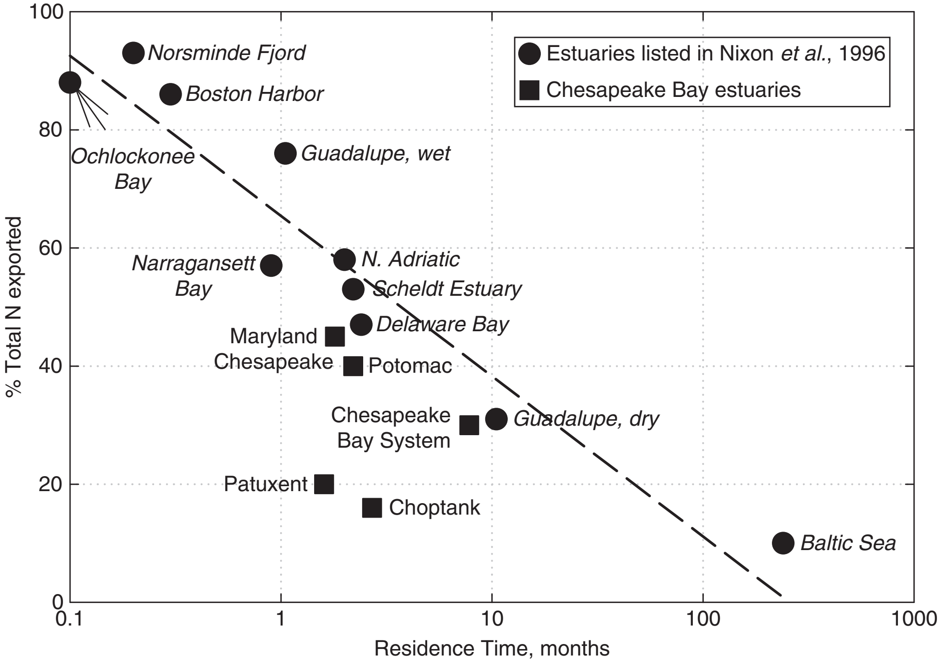

Figure 18.13 Scatter plot of percent N exported versus water residence time for a variety of estuarine ecosystems. Figure was re-drawn from Nixon *et al.* (1996). Patuxent and Choptank Rivers, tributaries of Chesapeake Bay, were not included in the original analysis. Data for those systems were from Boynton *et al.* (1995) and Fisher (unpublished data).

It appears that Chesapeake Bay and its tributary estuaries tend to remove a higher fraction of N loads than expected from the estimated water residence times (Fig. 18.13). Some of these differences may simply be the result of accumulated errors in developing N-budgets. However, Chesapeake Bay is a sediment-rich and eutrophic system with abundant suspended PN and sediment concentrations to facilitate burial. Of the estuaries examined by Nixon *et al.* (1996), only the Chesapeake systems had substantial N-burial losses, probably because of these features and moderately long water residence times. In addition, many Chesapeake Bay tributaries (e.g., Patuxent and Choptank) that export a small fraction of their N load have large areas of low-salinity tidal marshes which also sequester substantial amounts of both N and P (Greene, 2005b; Merrill, 1999). Thus, it's possible that some estuarine communities, such as those associated with tidal marshes and seagrass beds, may modify relative N export characteristics (Valiela *et al.*, 2001). To expand our understanding of N dynamics in estuaries, there is a clear need for more direct calculations of N exchange with seaward waters and better estimates of other loss terms including burial and denitrification.

3.4. Ecosystem metabolism: Interactions with nitrogen cycling

Under steady-state conditions, the balance between inorganic N inputs and losses for an estuary is directly related to the net production (or consumption) of organic matter in the associated ecosystem, where net organic production and net fluxes of inorganic N are inversely related. Net ecosystem production (NEP) is supported by net uptake of inorganic N, and conversely, net consumption of organic matter results in net release of inorganic N. NEP, which is defined as the balance between gross primary production (P_G) and community respiration (R_C) of organic carbon, provides a measure of the excess production or consumption resulting in changes in internal storage or net export or import across the system boundaries (Fisher and Likens, 1973; Odum, 1956). Ecosystems with positive NEP are considered autotrophic, while those with negative NEP are considered heterotrophic. Although P_G tends to equal R_C (NEP $\approx$ 0) at large scales, imbalances between P_G and R_C at smaller scales support functional coupling between adjacent habitats through exchanges of organic carbon and inorganic nutrients (e.g., Hopkinson and Vallino, 1995; Kemp *et al.*, 1997; Smith and Hollibaugh, 1997).

NEP can be calculated using different methods including long-term continuous records of dissolved oxygen or inorganic carbon (relative to saturation concentrations) at diel or seasonal scales (e.g., Howarth *et al.*, 1992), and summation of individual production and respiration measurements broadly representing temporal and spatial scales and major habitats (e.g., Kemp *et al.*, 1997). NEP can also be computed using estimates of the net balance between imports and exports of DIP (e.g., Smith, 1991), where rates are converted from phosphorus to carbon units assuming a fixed stoichiometry for primary production and nutrient recycling (e.g., C:N:P = 106:16:1). Conversely, NEP can be converted to nitrogen units using these stoichiometric assumptions; however, the net balance of DIN will also be affected by two important processes involving nitrogen gas production and consumption—denitrification and nitrogen fixation, respectively (e.g., Nixon and Pilson, 1984). In fact, rates of NEP and related biogeochemical fluxes have been estimated for many estuaries and coastal bays worldwide combining simple water- and salt-balance models that compute advective and diffusive solute transport with data for DIN and DIP time-space distributions to infer non-conservative net fluxes as residuals in dynamic nutrient budget calculations (http://wwwold.nioz.nl/loicz/). Comparative analyses of these rates suggest broad regional relationships with hydrology and watershed development (Smith *et al.*, 2003).

Estimates of NEP can also be made using time-varying water/salt balance calculations for an estuarine water volume segmented into two-layers and multiple regions (or boxes) along the salinity gradient (Hagy *et al.*, 2000). Such a ‘‘box-model’’ was used to compute net non-conservative fluxes for nutrients and dissolved oxygen (O_2, corrected for air-sea exchange) in the Patuxent River estuary, USA (Kemp *et al.*, 1999; Testa and Kemp, 2005). The inherently tight coupling between organic production (NEP) and N cycling can be seen in the highly correlated patterns of annual mean rates of net O_2 and DIN flux along the estuarine gradient for surface and bottom layers in hydrologically contrasting years (Fig. 18.14). In surface layers, interannual and longitudinal variations in DIN uptake generally correspond to patterns in net O_2 production, while in bottom layers, trends of net O_2 consumption appear as a mirror image of net DIN production rates. Bottom layer DIN fluxes are inversely correlated to O_2 fluxes ($r^2 = 0.81$); however, trends are complicated because negative fluxes in low salinity estuarine regions are from high water column nitrate concentrations diffusing into sediments to support denitrification, while positive net fluxes in the more saline regions are primarily due to ammonium efflux from decomposing organic matter in sediments.

Whereas annual rates of primary production tend to be regulated by inputs of total nitrogen for many coastal ecosystems (e.g., Boynton *et al.*, 1982; Nixon *et al.*, 1986), it appears that NEP (NEP $= P_G - R_C$) is controlled more by the balance between inputs of DIN and total organic nitrogen (TON) or carbon (TOC), where DIN inputs stimulate P_G, and TON (or TOC) inputs support R_C (Kemp *et al.*, 1997). Comparative analysis of NEP calculations and loading rates for five estuaries and for mesocosms (MERL; Oviatt *et al.*, 1986) at different nutrient treatments reveals a consistent relationship between NEP and the DIN:TOC loading ratio (Fig. 18.15). While strong relationships were evident for NEP from controlled experimental systems and for long term average rates in specific estuaries, substantial year-to-year variations in NEP are often evident for specific estuarine ecosystems. Such variations in metabolic rates may be related to fluctuations in climatic conditions that regulate, for example, inputs of organic matter from adjacent coastal upwelling regions (e.g., Smith and Hollibaugh, 1997), or river flow and associated nutrient loading and water residence time (Fig. 18.15, note differences in net fluxes for high and low flow years, and interannual variability in NEP in figure inset). Values for P_G and R_C computed from continuous diel O_2 measurements for a range of shallow North American coastal ecosystems revealed that NEP was generally negative (i.e., net heterotrophic), was responsive to climatic variations, and was related to N inputs (Caffrey, 2004). The heterotrophic nature of NEP in many coastal ecosystems combined with the correspondence between biogeochemical fluxes of C and N have been interpreted to suggest that N cycling, in general, and denitrification, in particular, may actually be limited by C availability (Smith and Hollibaugh, 1989). This is in contrast to the conventional view that carbon production and consumption are limited by N availability. In summary,

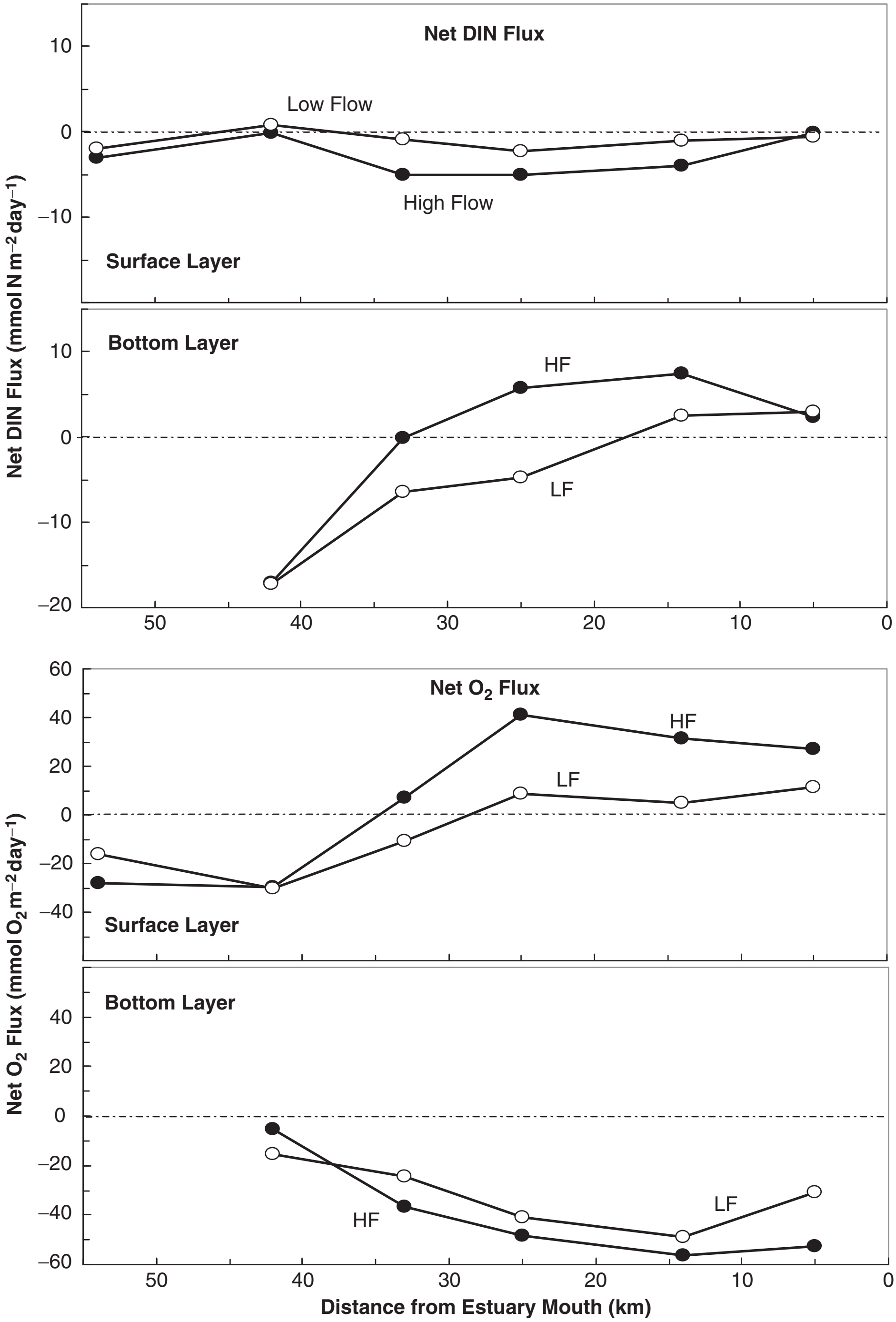

Figure 18.14 Net non-conservative biogeochemical fluxes of dissolved oxygen (O_2) and dissolved inorganic nitrogen (DIN) calculated using a box-model (Hagy *et al.*, 2000) for six regions and two vertical layers defined along the Patuxent River estuary for relatively wet (2000) and dry (2002) hydrologic years. Fluxes were estimated as residuals in mass-balance calculations for monitored O_2 and DIN concentrations (Kemp *et al.*, 1999).

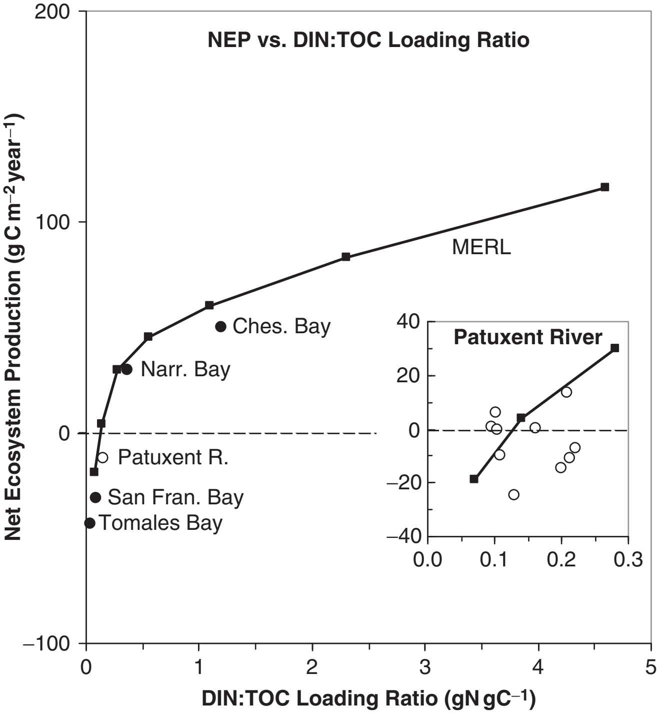

Figure 18.15 Comparative analysis of net ecosystem production for estuaries in relation to loading ratio for DIN:TOC. Data sources are: for MERL mesocosms (Oviatt *et al.*, 1986), for Narragansett Bay (Nixon *et al.*, 1995), for Tomales Bay (Smith and Hollibaugh, 1997), for San Francisco Bay (Jassby *et al.*, 1993), for Chesapeake Bay (Kemp *et al.*, 1997), and for Patuxent River estuary in 1985–1994 (Kemp *et al.*, 1999). Figure was adapted from Kemp *et al.* (1997). The DIN:TOC load ratio was based on external inputs of DIN ($NO_3 + NO_2 + NH_4$) and Total Organic Carbon (TOC) to each site.

we conclude total primary production and net ecosystem production are tightly coupled to inputs and cycling of N in most coastal environments, and that these relationships vary with hydrologic and climatic conditions.

4. SEDIMENT-WATER SOLUTE FLUXES

One of the distinguishing features of estuarine ecosystems is their relatively shallow water depths compared to many lakes and the coastal ocean. One consequence of a short water column is that the upper photic waters that support primary production are closely connected to zones of nutrient remineralization in estuarine sediments. This results in strong benthic-pelagic (B/P) coupling, which is one of several reasons suggested for the high primary and secondary productivity of estuarine systems (Kemp and Boynton, 1992). While B/P coupling implies bi-directional influences, we focus here on benthic N cycling and the efflux of DIN across the sediment-water interface. During the past twenty years a substantial number of sediment-water flux measurements have been made in diverse estuarine and coastal marine systems, providing opportunity for a synthetic analysis. In the following section we consider ammonium effluxes because they have been widely measured and because NH_4 is usually the primary N compound released by sediments. However, we also included oxygen and DIP fluxes because they are also widely measured and because O_2, DIP and NH_4 fluxes are stoichiometrically linked in complex ways. We recognize that other N forms, such as NO_3, can occasionally play a significant role in sediment nutrient dynamics. In recent years, a growing number of sediment-water fluxes have been measured in shallow, clear-water systems where sediments are in the photic zone (e.g., Eyre and Ferguson, 2002; McGlathery *et al.*, 2001; Reay *et al.*, 1995; Rizzo *et al.*, 1992; Rysgaard-Petersen *et al.*, 1994; Tyler and McGlathery, 2003). N cycling under those conditions is apparently even more complex, with benthic photosynthesis supporting N-assimilation, shifting redox conditions and associated biogeochemical processes. A detailed discussion of these data can be found elsewhere in this book (Chapter 23 by McGlathery, this volume). Finally, we did not review DON fluxes associated with estuarine sediments because these have not been routinely measured and because Bronk and Steinberg (Chapter 8, this volume) and Joye and Anderson (Chapter 19, this volume) address this issue in detail.

4.1. Overview of flux magnitude

Sediment-water fluxes of ammonium (NH_4), dissolved oxygen (O_2), and dissolved inorganic phosphorus (PO_4) were organized based on data from 52 studies (6, 19, 26, and 1 from the 1970s, 1980s, 1990s and 2000s, respectively) conducted in 48 estuarine and coastal marine areas. A total of 701 flux measurements were included in the summary developed by Bailey (2005). Measurements included those made *in situ* or with ship-board or laboratory sediment core incubations. In all cases, measurements of analyte concentrations (O_2, NH_4, and PO_4) were made during an incubation period in the dark at ambient water temperature, and fluxes were computed using concentration temporal rates of change. Studies using modeling techniques or fluxes estimated from sediment pore water concentrations were not included.

Mean values of flux magnitudes and ratios exceeded median values (Table 18.4); there were a small number of large values for each of these fluxes (Fig. 18.16A).

Table 18.4 Summary of Net Sediment-Water Oxygen and Nutrient Exchanges and Flux Ratios from 48 Estuarine and Coastal Ecosystems Developed by Bailey (2005)

Type of flux or flux ratio	Minimum	Maximum	Mean	Median	*n*
NH_4	−83	2700	125	42	641
PO_4	−231	900	22	4.2	506
O_2	0	−18229	−1302	−781	554
N: P	0	193	13	7.8	369
O: N	0	1450	63	24	413

All measurements were made in environments where the sediments were aphotic and all sediment incubations were made in the dark. Flux units are: umol O_2, N or P m^{-2} h^{-1}; N: P and O: N ratios atomic basis. Negative values indicate fluxes into sediments.

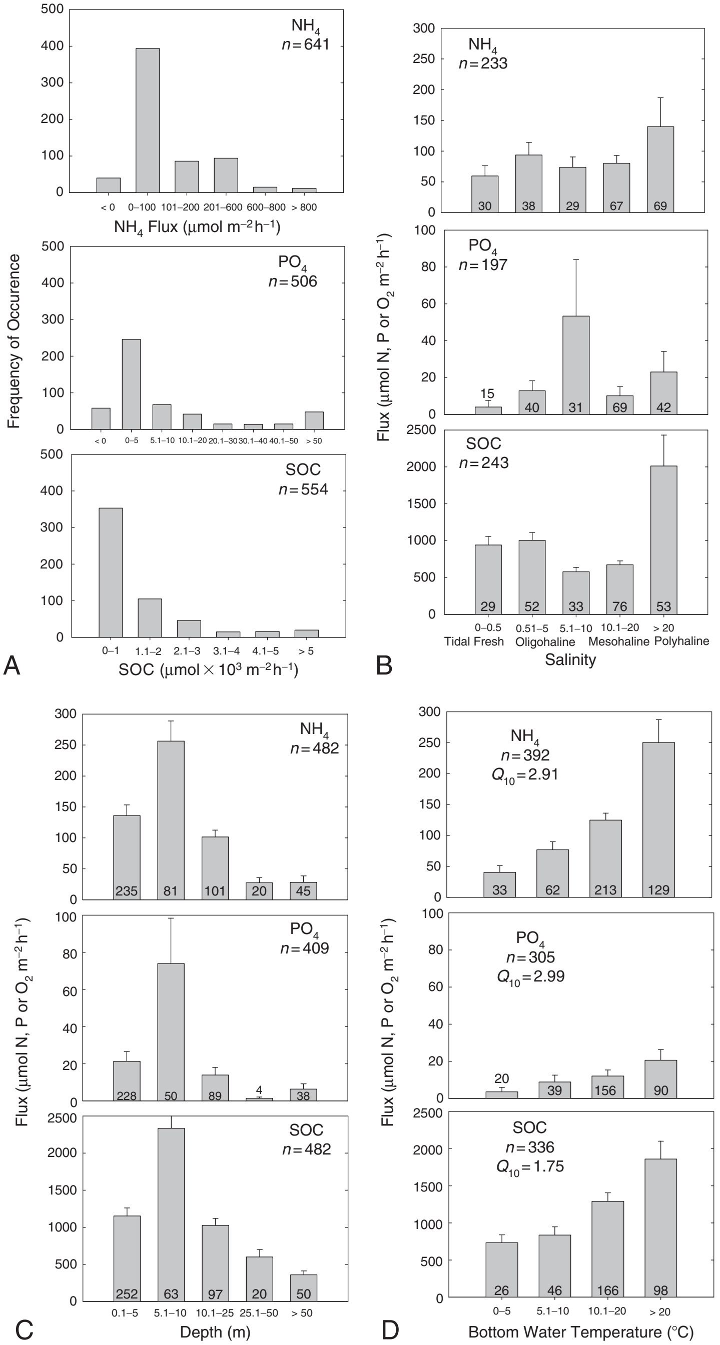

Figure 18.16 A summary of sediment-water NH$_4$, PO$_4$ and sediment oxygen consumption (SOC) rates, including: (A) frequency histogram of rates; (B) rates as a function of salinity regime; (C) rates as a function of system depth; (D) rates as a function of temperature. Data were organized by Bailey (2005).

Sediment oxygen consumption (SOC) rates ranged from 0 to 18,229 μmol m^{-2} h^{-}, ammonium fluxes from −83 to 2700 μmol m^{-2} h^{-1} and phosphate fluxes from −231 to 900 μmol m^{-2} h^{-1}. Flux ratios are also of interest because they can provide an indication of active sediment biogeochemical processes. Median values of N: P and O: N flux ratios were lower and higher, respectively, than would be expected based on Redfield phytoplankton composition ratios (N: P $\sim$ 16; O: N $\sim$ 13.3). Both ratios suggest less N being recycled relative to recycled P and to oxygen consumption rates. While several explanations are possible, much of this pattern is probably attributable to loss of N-solutes via nitrification-denitrification in estuarine sediments (e.g., Jenkins and Kemp, 1984; Rysgaard-Petersen *et al.*, 1994; Seitzinger, 1988).

4.2. Spatial patterns of flux

All fluxes tended to be higher in saltier than in fresher waters (Fig. 18.16B). Although one might anticipate that NH_4 and SOC fluxes would be inversely related to salinity with highest values closest to terrestrial organic matter and nutrient sources, this was not the case. Apparently, more phytoplanktonic debris, which is more labile with lower C:N ratios, tends to be the dominant source of organic matter fueling benthic processes in higher salinity zones. On the other hand, DIP efflux from sediments tended to peak in the low mesohaline (salinity = 5–10) region. This is probably a manifestation of both loosely sorbed P being released into solution as a consequence of increased salinity (Froelich, 1988) and of the dissolution of iron-phosphate complexes after chemical reduction of iron and precipitation of iron sulfides in anaerobic sediments (Jensen *et al.*, 1995; Krom and Berner, 1980).

In general, SOC tends to decline with water depth (e.g., Hargrave, 1973; Kemp and Boynton, 1992; Kemp *et al.*, 1992), as plankton respiration causes a smaller percentage of sinking organic matter to reach the bottom due to longer transit times in deeper water columns. Efflux of NH_4 from sediments has previously been related to water column depth (Harrison, 1980) across large gradients (10–2000 m). We found a generally similar response for NH_4, PO_4, and SOC fluxes (Fig. 18.16C) for a relatively small depth range (0.2–50 m). Fluxes were 5 to 10 times higher in water of 5–10 m depth than in waters greater than 50 m depth, consistent with earlier reports for SOC. However, mean fluxes in the dark were lower at very shallow depths (0.2–5 m). The shallow water sediments are typically within the zone where autotrophic processes tend to dominate sediment biogeochemistry, with high rates of N and P assimilation by benthic algae and seagrasses and oxidized sediments which promote adsorbtion and precipitation of PO_4 and coupled nitrification-denitrification of N. Thus, NH_4 and PO_4 effluxes tend to be low in these shallow sediments. In addition, sediments and organic matter may be exposed to resuspension via wave action and the less dense labile organic particulates transported to deeper waters where they are remineralized. The flux-depth pattern observed with our large data set is not consistent with several other analyses including those of Nixon (1981) and Seitzinger and Giblin (1996) where depth ranges of 3–70 m and <200 m, respectively, were examined and did not exhibit strong relationships with depth.

4.3. Regulation of sediment–water fluxes

There are many factors that may play important roles in regulating sediment biogeochemical processes and associated solute exchanges. There is a substantial literature concerning this topic, extending back several decades. The list of potential influencing factors includes temperature, activities of infaunal communities, redox conditions near the sediment-water interface, solute concentrations in overlying water, and rates of organic matter supply. Effects of infauna can be both direct (i.e., excretion) and indirect (i.e., burrowing, pumping, and stimulation of microbial communities). For example, Banta *et al.* (1995), Flint and Kamykowski (1984), Hammond *et al.* (1985), Kanneworff and Christensen (1986), and Webb and Eyre (2004) reported a variety of macrofaunal influences on sediment-water exchange rates and other processes. Others have reported on the influence of redox and water quality conditions on sediment processes (e.g., Sundby *et al.*, 1992). The challenge of quantitative modeling of sediment-water processes and associated interactions was captured in a recent book by DiToro (2001).

Previous studies have concluded that, ultimately, organic matter supply rate to sediments was the overarching factor regulating sediment biogeochemistry and solute flux across the sediment-water interface. For example, comparative analysis among diverse estuarine systems indicates that benthic respiration rates are highly correlated with organic matter production rates (Nixon, 1981). The relationship appeared to be linear across a very large range of primary production rates ($\sim$75–1400 g C m^{-2} $year^{-1}$), including data from Chesapeake Bay (Kemp and Boynton, 1992). In northern European waters, rates of sediment respiration and ammonium and phosphorus fluxes tend to respond rapidly to deposition of spring and autumn algal blooms (Graf *et al.*, 1982; Jensen *et al.*, 1990). Although temperature appears to affect response time, similar relationships have been reported for sediment anaerobic respiration in North American systems (Marvin-DiPasquale *et al.*, 2003; Sampou and Oviatt, 1991).

Interacting effects of organic matter supply and temperature are illustrated with two examples from Chesapeake Bay aphotic sediments. In the first case (Cowan and Boynton, 1996), sediment chlorophyll *a* concentration (as an index of recent organic deposition) was related to sediment-water NH_4 fluxes measured during three years at three stations along the estuarine salinity gradient (Fig. 18.17). These stations varied substantially in terms of mean depth, O_2 conditions, sediment type, and macrofaunal characteristics; the strength of the observed relationship, therefore, emphasizes the overall importance of organic matter supply. A second point of interest is the lag time used in this analysis. Specifically, sediment chlorophyll *a* concentrations were averaged from just prior to spring bloom deposition through the summer period, while NH_4 fluxes were averaged from mid-spring through summer. Biogeochemical processes in this system, which has a large annual temperature range (0–33°C), are apparently not adapted to cold water (Sampou and Kemp, 1994). It is argued that sediment respiration and nutrient remineralization respond to spring bloom deposition and labile organic matter accumulation primarily after temperature increases beyond 10°C (Cowan and Boynton, 1996). Thus, there is a period of organic matter

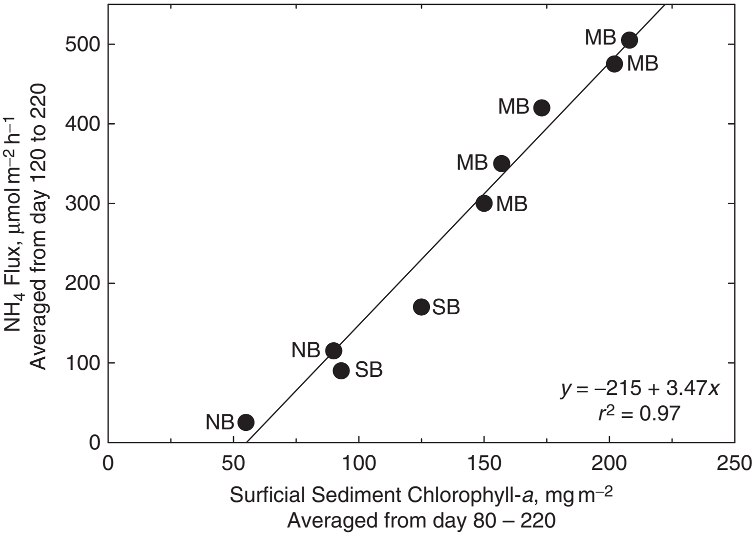

Figure 18.17 A scatter plot of sediment NH$_4$ fluxes versus surface sediment chlorophyll *a* concentration collected for several years at three sites along the salinity gradient of Chesapeake Bay. Note that sediment chlorophyll *a* data were averaged from late winter through summer while sediment fluxes were averaged from late spring through summer. Figure was redrawn from Cowan and Boynton (1996). NB–Northern Bay (oligohaline); MB–Mid Bay (mesohaline); SB–South Bay (polyhaline).

loading to sediments followed by a period of NH$_4$ release. Other investigators have found a more immediate response to temperature (e.g., Banta *et al.*, 1995). However, the importance of organic matter supply rate is clearly evident in these results. The second example is from the Patuxent River, where multiple NH$_4$ flux measurements were made during three summer periods, all within the mesohaline region of the estuary (Stankelis *et al.*, 1999). Water column and sediment characteristics were also measured at flux site locations and a reasonably simple regression model was developed in which sediment chlorophyll *a*, as an index of labile organic matter supply, again played an important part (Fig. 18.18). An additional twist in this analysis was the apparent role played by sediment redox conditions. The model indicated that as sediment redox conditions became more positive, less NH$_4$ was released. This is consistent with the idea that sediment N is more likely to be nitrified when sediments are oxidized (Kemp *et al.*, 1990; Rysgaard-Petersen *et al.*, 1994).

We also examined flux data with respect to water temperature at the time of measurement using the sediment-water flux data set developed by Bailey (2005; Fig. 18.16D). In all cases there were sharp increases in rates with increased temperature. Estimated Q_{10} (0–30°C) values for NH$_4$, PO$_4$ and SOC fluxes were 2.9, 3.0, and 1.8, respectively. It is also useful to note there is considerable bias in the temperature range in which these measurements are made. Less than 10% of the reported rates were from temperatures <5°C, and only a slightly higher percentage were from temperatures of 5–10°C. About 50% of all measurements

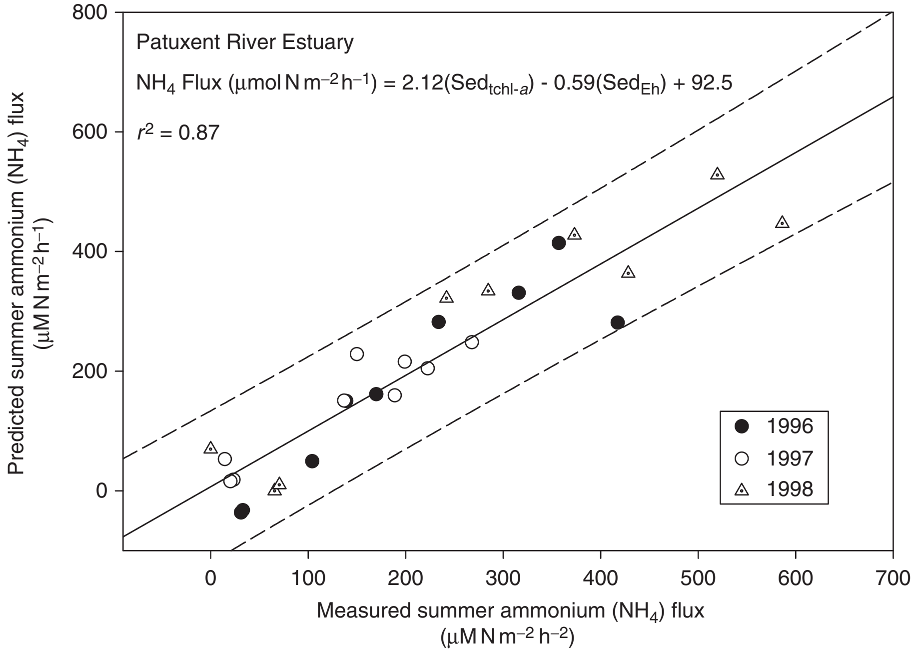

Figure 18.18 A scatter plot of predicted versus measured NH_4 fluxes for the mesohaline region of the Patuxent River estuary. Data and figure are from Stankelis *et al.* (1999).

were made at temperatures between 10°C and 20°C, a fact that suggests a *Goldilocks and the Three Bears* approach to ecology wherein measurements were made when it was neither too hot nor too cold, but just right (Brett, 1987). To examine the influence of temperature on sediment fluxes in more detail, we organized a rare 9 year time-series of sediment NH_4 fluxes collected from two Chesapeake Bay tributaries- the Potomac and Patuxent River estuaries (Boynton and Rohland, 1998). For comparison, monthly NH_4 fluxes were expressed as percent of maximum flux observed during each year, averaged by month for the 9 year record, and then plotted as a function of average temperature at the time of measurement (Fig. 18.19). Results from the heavily nutrient enriched Potomac and moderately enriched Patuxent indicated increasing fluxes with increasing temperature through mid-summer but then sharply reduced fluxes at comparable or slightly higher temperatures through late summer and fall. A similar pattern was reported from a site in Chesapeake Bay (Cowan and Boynton, 1996). The substantial differences in flux magnitude before and after July indicate that other factors, such as supply of labile organic matter, limit remineralization in late summer and autumn. However, there appear to be a variety of seasonal patterns of sediment fluxes among estuaries. For example, Banta *et al.* (1995) and Nixon *et al.* (1976) found strong relationships between temperature and sediment ammonium fluxes in Buzzards Bay and Narragansett Bay. The seasonal pattern of sediment denitrification may also strongly influence the pattern of sediment ammonium fluxes (Hopkinson *et al.*, 1999).

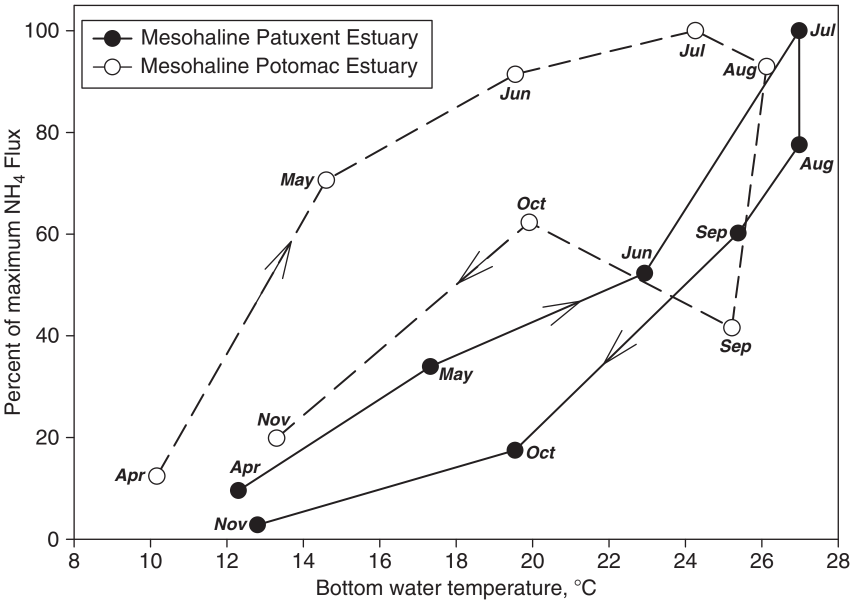

Figure 18.19 A scatter plot of sediment NH_4 fluxes as a function of temperature from two tributary rivers of Chesapeake Bay. NH_4 fluxes were based on 9 years of monthly samples. Fluxes were expressed as a percent of the maximum flux observed in each year and then averaged, again by month, for all years. Temperature was the average temperature during each month of the 9 year record at each site. The Potomac site was very nutrient enriched and the Patuxent site was moderately enriched. Data were from Boynton and Rohland (1998).

5. NITROGEN AND PRIMARY PRODUCTION

In many estuarine systems primary production by phytoplankton and other autotrophs is affected by N inputs and concentrations (e.g., Cloern, 2001; Howarth, 1988; Kelly, 2001; Nixon, 1992; Smith, 2003). For this review, we have compiled estimates of annual primary production and simple models used to relate production to nutrient conditions. We also discuss the evolution of thinking concerning nutrient limitation of pelagic primary production in estuaries. Finally, we review the conceptual models concerning benthic and pelagic primary production and consider the influence of N on these different autotrophic components.

5.1. Phytoplankton primary production

Annual rates of phytoplankton primary production from 120 different estuarine and coastal marine systems were organized in a frequency plot (Fig. 18.20). The most frequently encountered rates were those between 100 and 300 g C m^{-2} $year^{-1}$, corresponding to mesotrophic status in the classification suggested by Nixon (1995). Despite very real concern about increasing eutrophication of coastal systems, only 32%

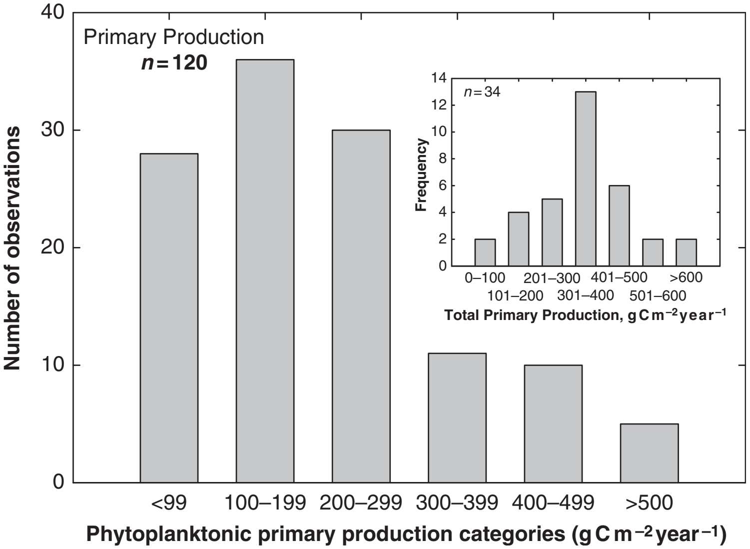

Figure 18.20 Frequency distribution of annual phytoplankton primary production rates for a selection of estuarine and coastal marine systems. Data were from Borum and Sand-Jensen (1996), Boynton *et al.* (1982), Chen *et al.* (2000), Cloern (2001), Conley *et al.* (2000), deJonge *et al.* (1994), Harding *et al.* (2002), Kelly (2001), Nixon (1997), and Pennock and Sharp (1986). Inset diagram shows frequency distribution for total primary production (pelagic plus benthic) for a limited number of estuaries. Inset data were from Borum and Sand-Jensen (1996).

of these systems were in the eutrophic or hypertrophic categories. It is unclear, however, how representative this sample is of estuarine systems worldwide. It is almost certain that vast amounts of data remain to be mined from unpublished sources and that incorporation of this material might substantially change the observed pattern. In addition, most estimates of primary production are estimates of pelagic primary production; few included benthic primary production, which is especially important in shallow systems. We used the summary of total system (pelagic plus benthic) primary production compiled by Borum and Sand-Jensen (1996) and examined categories of production relative to trophic state (Fig. 18.20 inset). In this smaller sample, rates were generally higher, as expected, with 68% of the sites having annual productivity rates greater than 300 g C m^{-2} $year^{-1}$. Most of these sites were shallow, even by estuarine standards, and exhibited very high production rates, clearly indicating the importance of benthic primary producers. Borum and Sand-Jensen (1996) also pointed out that it was rare for both benthic and planktonic rates to be high in the same system, and indicated that conditions which enhance one group of primary producers tend to inhibit the other.

5.2. Statistical models of nitrogen and production

We also compiled reports of statistical models developed to relate primary production or algal biomass to N (Table 18.5). All but one of these were generated during the last two decades, and the models take a variety of forms, for example, using N

Table 18.5 A summary, by date of publication, of statistical models relating phytoplankton primary productivity or biomass to nitrogen (concentration or loading rates) or other variables

Location	Independent variable, *X* (units)	Dependent variable, *Y* (units)	Predictive equation	r^2/n	Reference
Multiple estuaries	TN loading (g N m^{-2} $year^{-1}$)	Phytoplk Prod (g C m^{-2} $year^{-1}$)	$Y = 25 + 13X$	0.60/14	Boynton *et al.*, 1982
San Francisco Bay other estuaries	Composite parameter $X = f(B, Z_p, I_0)$	(mg C m^{-2} $year^{-1}$)	$Y = 15 + 0.73X$	0.82/211	Cole and Cloern, 1987
Narragansett Bay and Univ RI MERL	Composite parameter $X = f(B, Z_p, I_0)$	(g C m^{-2} $year^{-1}$)	$Y = 220 + 0.70X$	0.82/1010	Keller, 1988
Multiple estuaries and Univ RI MERL	DIN-loading (mol N m^{-2} $year^{-1}$)	(g C m^{-2} $year^{-1}$)	$\log Y = 0.44 \log (X) + 2.33$	0.93/19	Nixon *et al.*, 1996
Multiple estuaries	TN loading (g N m^{-2} $year^{-1}$)	(g C m^{-2} $year^{-1}$)	$Y = 244 + 175 \log (X)$	0.36/51	Borum and Sand-Jensen, 1996
Boston Harbor	Composite parameter $X = f(B, Z_p, I_0)$	(mg C m^{-2} $year^{-1}$)	$Y = 285 + 0.79X$	0.66/12	Kelly and Doering, 1997
Waquoit Bay system	Annual average DIN conc (μM)	(g C m^{-2} $year^{-1}$)	$Y = 60.9 + 13.96X$	0.61/12	Valiela *et al.*, 2001
Chesapeake Bay	TN(x_1), TP(x_2) load (kg mol^{-1})	(g m^{-2} $year^{-1}$)	$Y = 335 + 18.9X_1 - 164X_2$	0.67/11	Harding *et al.*, 2002

Multiple estuaries	DIN (m M m^{-3}); tidal range (m)	Phytoplk Biomass (μg I^{-1})	na; positive slope	na/163	Monbet, 1992
Multiple systems/ MERL	DIN input (mmol m^{-3} year^{-1})	(μg I^{-1})	na; positive slope	na/34	Nixon, 1992
Chesapeake Bay mesohaline region	River flow (m^3 day^{-1}) (proxy for N-load)	(kg estuary^{-1})	na; positive slope	0.70/34	Harding *et al.*, 1992
Maryland lagoons	TN load (g N m^{-2} year^{-1})	(μg I^{-1})	$Y = 16.9 + 0.70X$	0.96/9	Boynton *et al.*, 1996
Danish coastal waters	TN concentration (μg I^{-1})	(μg I^{-1})	na; positive slope	0.64/168	Borum, 1996
Canadian estuaries	TN concentration (μg I^{-1})	(μg I^{-1})	$\log Y = -4.06 + 1.78 \log X$	0.72/15	Meeuwig, 1999
Chesapeake Bay and Tributaries	Scaled TN load (mg N m^{-2} year^{-1}) (R_{time}, years)$^{-1}$	(mg m^{-2})	$Y = 18.9 + 0.078X$	0.82/17	Boynton and Kemp, 2000
Danish estuaries	TN concentration (μg N I^{-1})	(μg I^{-1})	$\text{In}(Y) = 0.96\ \text{In}\ (X) - 4.19$	0.30/1347	Nielsen *et al.*, 2002

concentration or loading rate as an independent variable. Most models were computed on annual time scales, and for several it was unclear how temporal and spatial variability was taken into account. Sample size used to develop these models varied widely, and some were based on multi-system comparisons while others were based on multi-year data collected for one system. Given the myriad factors known to influence production and algal biomass accumulation, it is impressive that N alone was able to account for a large portion of the variability of phytoplankton production or algal biomass.

There are, of course, some serious limitations with these analyses. These are basically correlations and thus do not demonstrate causation; results may be related to some other co-variate. More importantly, other possible explanations for production or biomass variability were not always thoroughly examined (Peters, 1991). For example, in some of these papers it appeared that N was assumed, *a priori*, to be the key explanatory variable, while other factors, such as P or light availability, were not examined with equal rigor. One could make the case that sufficient data are now available to initiate a more comprehensive, comparative synthesis of estuarine primary production (both pelagic and benthic) that considers a wider selection of independent variables and uses dimensional scaling to the extent needed to ensure adequate comparability among different estuarine locations. In short, estuarine ecologists need to take a lesson from the limnologists who began doing just that some 30 years ago (e.g., Vollenweider, 1976) and developed tools useful for both scientific understanding and for lake management.

5.3. Nutrient limitation

The question of nutrient limitation is fundamentally important for understanding controls on estuarine production and practically important for understanding how to mitigate eutrophication. In recent decades, nutrient limitation concepts have been better defined, explanations for differences in nutrient limitation among systems have been clarified, and experimental approaches have been organized in a heiarchial suite, from short-term small-scale bioassays, to intermediate-scale mesocosm studies, to whole-system biogeochemical analyses. The history of development of nutrient limitation studies has been reviewed (Howarth, 1988) and more recent studies have discussed the use of data from these studies for nutrient management in such areas as Chesapeake Bay and the Baltic Sea (Elmgren and Larsson, 2001; Malone *et al.*, 1993). The basic story is summarized below.

In the 1970s limnologists produced convincing evidence that for many lakes P was the important limiting nutrient (e.g., Schindler, 1977). With the growing sense that estuaries and coastal waters were showing signs of serious nutrient-based eutrophication, the lake model was assumed to apply. However, contemporaneous studies in coastal areas (e.g., Ryther and Dunstan, 1971) suggested that N was more important than P in estuarine and coastal systems, and studies conducted during the 1980s generally supported that view (e.g., Caraco *et al.*, 1987; D'Elia *et al.*, 1986; Graneli, 1987). P limitation in lakes had been demonstrated at various scales of complexity/realism (i.e., bioassays, mesocosms and whole-lake experiments), but the same degree of testing had not been completed in estuaries and hence the N conclusion needed to be viewed with caution (Hecky and Kilham, 1988). For many estuaries, however, long-term field studies (e.g., Jordan *et al.*, 1991), multi-year, system-wide bioassay studies (e.g., Fisher *et al.*, 1992, 1999), whole-year mesocosm experiments (D'Elia *et al.*, 1986; Harrison *et al.*, 1990; Oviatt *et al.*, 1995) and some whole-system experiments (Conley *et al.*, 2000; Elmgren and Larsson, 2001; Paerl *et al.*, 2004) have been completed, and the emerging story is more complete and complex.

In general, pelagic estuarine productivity tends to be limited by N; however, light, P, Si and other factors also play into the story. Nitrogen limitation appears to be more often the case in higher salinity than in tidal fresh waters and more intense in summer/fall than in winter/spring. These temporal/spatial patterns tend to parallel trends in dissolved inorganic nutrient ratios (DIN:DIP) in the water column which, in turn, are often reflective of the nutrient composition of inputs. Many authors indicate P limitation associated with high N: P ratios (>90, Caraco *et al.*, 1987; >90, D'Elia *et al.*, 1986; >80, Harrison *et al.*, 1990; >60, Kemp *et al.*, 2005; >30, Pennock and Sharp, 1994), a condition that often occurs during winter/spring in estuaries with significant freshwater inflows not dominated by sewage. Dodds (2003) reviewed use of DIN: DIP ratios as an indicator of nutrient limitation and argued for the use of TN:TP ratios rather than the inorganic ratios more commonly used in estuarine analyses. When N supply is extremely high (e.g., south China coast), P may be more generally limiting, but again, it seems probable that outside the plume of low salinity, N-rich water, limitation switches back to N (Harrison *et al.*, 1990). There is also some empirical evidence that P limitation is a more general feature of warm temperate embayments, such as those along the Gulf of Mexico (e.g., Murrell *et al.*, 2002).

In overview, the emerging picture is one of a mosaic of general N limitation, but with substantial time-space regions where productivity is limited by P and other factors. This description is certainly consistent with a view of estuaries as gradient-rich, dynamic ecosystems that lie between the land and the sea and are influenced by both. Given the diversity of responses reported for estuaries, a uniform nutrient management directive does not seem possible. In large temperate coastal systems that include a full salinity gradient from tidal fresh to polyhaline, it may be prudent to consider a "duel-nutrient reduction strategy" wherein both N and P loads are reduced. This approach ensures that eutrophic conditions will be reduced both in tidal freshwater areas where P tends to be limiting, and in meso- and polyhaline areas where N is more important (Conley, 1999; Elmgren and Larsson, 2001; Fisher *et al.*, 1999; Paerl *et al.*, 2004).

5.4. Benthic autotrophs and nitrogen

Although the majority of the discussion regarding N-productivity interactions has focused on phytoplankton, N is also an important control on benthic primary production in estuarine ecosystems. During the past two decades, there has been much research examining how nutrient additions have contributed to global seagrass decline (e.g., Duarte, 1995; Kemp *et al.*, 1983). The cause-effect linkage of seagrass decline and nutrient additions typically involves increased phytoplankton standing stocks and associated reduced water transparency (e.g., Nielsen *et al.*, 2002).

In addition, in some areas, enhanced epiphytic growth on seagrass leaves further reduces light availability, eventually leading to loss of this community (e.g., Taylor *et al.*, 1995; Twilley *et al.*, 1985).

In other shallow ecosystems, macroalgae play a prominent role in the response to N addition: as nutrient inputs are increased, macroalgae first replaces seagrasses and then with further nutrient increases, macroalgae are themselves replaced by dense phytoplankton stocks (Valiela *et al.*, 1992). This sequence is modified by the influence of water residence time and the nutrient buffering influence of adjacent fringing ecosystems (e.g., Valiela *et al.*, 2001). Bowen and Valiela (2001) traced historical changes in N loads to a cluster of coastal embayments and reported a doubling of loads between 1938 and 1990, progressive increases in phytoplankton and macroalgae stocks and a decline in seagrass coverage. It is somewhat dispiriting to learn that seagrass declines, at least in these coastal systems, were associated with N loads as low as 3 g N m^{-2} $year^{-1}$, rates far lower than for many estuaries (Fig. 18.9). A series of papers concerning nitrogen effects on autotroph assembledges in Danish estuaries were especially comprehensive considering water residence times, nutrient demands, growth rates, C:N:P ratios and light requirements. (Borum, 1996; Borum and Sand-Jensen, 1996; Pedersen and Borum, 1996; Sand-Jensen and Borum, 1991). These studies found that nutrient enrichment changed plant community composition such that slow growing macro-algae were replaced by fast growing algal species, both of which rely primarily on water column rather than sediment nutrient sources.

In overview, several things seem clear. Very high primary production rates can be maintained in benthic dominated systems (Fig. 18.20, inset) with sufficient light reaching the bottom. Benthic autotrophs (microalgae, macroalgae and seagrass) are capable of obtaining N needed for growth either from sediment porewaters or from overlying water column pools depending on concentration gradients. There appears to be a generally predictable sequence relating predominant autotrophic groups to nutrient enrichment level. This sequence is likely related to competition for nutrients and light, where seagrasses dominate at one end of the gradient (low nutrients) because of their ability to tap deep sediment porewater nutrients, and phytoplankton dominate the other end (high nutrients) because of their ability, at high densities, to shade out benthic autotrophs.

6. NITROGEN AND SECONDARY PRODUCTION

Inputs and transformations of N and other nutrients directly influence production of all populations of consumer organisms, be they small or large. On one hand, nutrient additions generally result in increased primary production, which propagates forward to support increased growth of consumer populations, including fish. The amplitude of nutrient enrichment effects, however, tends to be damped as it is passed from one consumer population to the next, with responses being relatively large for primary producers, modest for herbivores, and small for top-carnivores (e.g., Micheli, 1999). On the other hand, spatial or temporal shifts in the abundance of fish and other consumers can result in marked effects on nutrient transport and recycling processes (e.g., Kitchell *et al.*, 1979). Primary production is passed on to diverse consumer organisms through feeding interactions and food-webs (e.g., Clarke, 1946; Lindeman, 1942). These webs can often be described with equivalent straight food-chains, where plants are consumed by herbivores, which are consumed by first-level carnivores, and so on (Ulanowicz and Kemp, 1979). Food-webs and food-chains are considered to be controlled by "bottom-up" or "top-down processes," depending on the relative responses to changes in nutrient inputs at the bottom or changes in carnivorous predation at the top, respectively (e.g., Carpenter *et al.*, 1985). Here, we address the double-edged question of how secondary production and nutrient cycling processes are related. We focus on N because it tends to be the limiting nutrient for primary production on annual time scales in most estuaries.

6.1. Effects of nitrogen enrichment on secondary production

It has been suggested by Caddy (1993, 2000) that nutrient enrichment affects secondary producers through a range of mechanisms that follow a sequence of three stages. At relatively low nutrient loading rates, the first stage involves enhanced production of demersal and pelagic species as a result of increased food availability. In the second stage, at moderate nutrient loading rates, benthic invertebrates and demersal fish tend to decline but planktonic consumers and pelagic fish species continue to increase with more nutrient additions. In the hypothesized third stage of this model, there is a general decline in total production of invertebrates and fish as water quality and habitat conditions become severely degraded. There is substantial direct evidence for the first two stages of this proposed sequence, while evidence for the third stage is more limited and indirect.

Comparative analysis of fisheries landings and primary production among diverse coastal systems (Nixon and Buckley, 2002) reveals a significant positive relationship (Fig. 18.21A). This may illustrate Caddy's first stage, where increasing inputs of nutrients support higher rates of primary production that in turn support higher rates of fish production and harvest. At least for herbivorous fish such as Atlantic menhaden, this relationship is supported by controlled experiments (Keller *et al.*, 1990) and bioenergetic models (Luo *et al.*, 2001) which indicate that production of estuarine fish tends to increase with nutrient enrichment. Although this relationship is impressive, there are key underlying assumptions which need to be considered. Perhaps the most obvious of these is the assumption that fisheries harvest provides a dependable index of fish production. The relationship (Fig. 18.21A) also suggests that exploited fish populations are generally food-limited and relatively unaffected by fishing mortality, conclusions that are difficult to reconcile with fundamental principles of fisheries science (e.g., Chesney *et al.*, 2000). Alternative explanations include the possibility that human population density (and associated nutrient loads) and fishing pressure are highly correlated when comparing different estuaries or regions. Consequently, densely populated coastal regions, which tend to have eutrophic estuarine waters and high rates of primary production, also support heavily exploited fisheries, often dominated by species feeding at lower trophic levels (e.g., Pauly *et al.*, 1998). Nevertheless, the strength of this relationship and the fact that similar patterns have been reported previously for lakes are undeniable (e.g., Nixon, 1988).

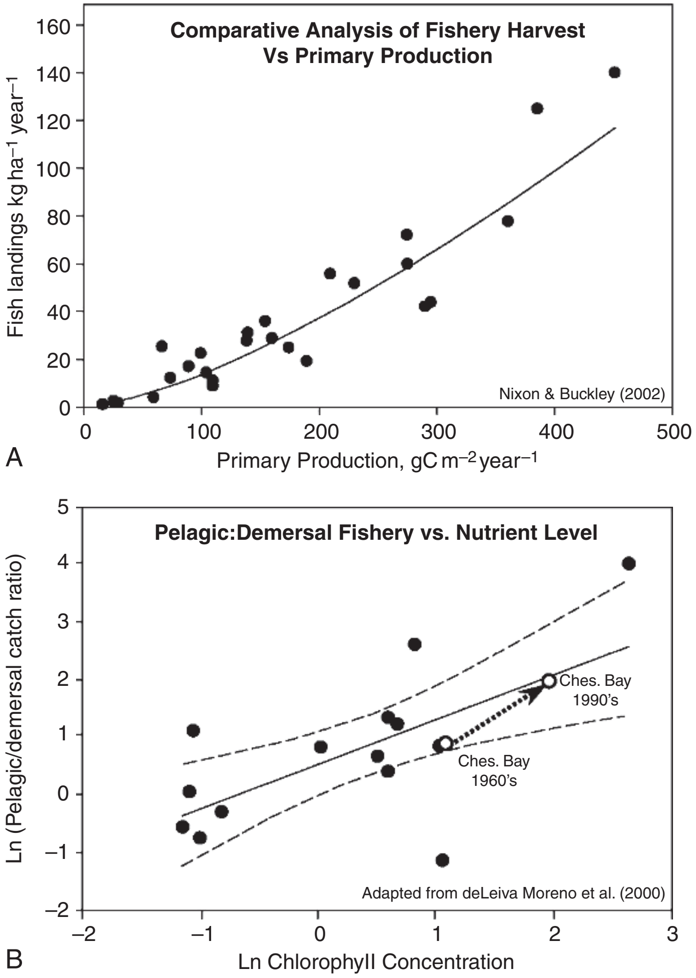

Figure 18.21 Comparative analyses of fisheries characteristics in relation to trophic status of estuarine and coastal ecosystems around the world: (A) fisheries harvest versus primary production (re-drawn from Nixon and Buckley, 2002); (B) ratio of pelagic-to-demersal fish caught in fishery plotted versus phytoplankton chlorophyll concentration (natural logarithm of both x and y variables). Figure 18.21 (B) was re-drawn from de Leiva Moreno *et al.* (2000) with Chesapeake Bay data added for two time periods.

Consistent with Caddy's second stage, recent data indicate that continued nutrient enrichment causes estuarine benthic habitats to become degraded, thereby contributing to marked shifts in food-web structure (e.g., Kemp *et al.*, 2005). For example, increased nutrient loading leads to decreased water clarity, which tends to cause loss of seagrass habitat in shallow areas (e.g., Duarte, 1995; Kemp *et al.*, 1983) and related reductions in fish and invertebrate production (e.g., Lubbers *et al.*, 1990). In some coastal lagoons, the loss of seagrass may be followed by outbreaks of dense benthic macroalgae stands with episodic hypoxic events that further degrade these habitats for fish and benthos (e.g., Deegan, 2002). Enhanced phytoplankton production from N enrichment can also degrade deeper estuarine habitats by inducing prolonged seasonal hypoxia and anoxia in stratified water columns (e.g., Hagy *et al.*, 2004). As a result of this deep-water hypoxia, the behavior of bottom-dwelling animal populations is altered (e.g., Brandt, 1993; Phil *et al.*, 1991) and their abundance, diversity and production tend to decline (Howell and Simpson, 1994; Kemp *et al.*, 2005). A major consequence of benthic habitat degradation is a general switch from food-webs dominated by demersal pathways under low N-loading to ones dominated by pelagic pathways in more eutrophic estuaries (e.g., de Leiva Moreno *et al.*, 2000). It appears that this trend is often reflected in fisheries harvests with the ratio of pelagic-to-demersal (P/D) catch being directly related to indices of nutrient loading such as phytoplankton abundance (Fig. 18.21B). Time-series fisheries data in Chesapeake Bay from 1960 to 2000 reveal a trend of generally increasing P/D ratio that parallels increases in nutrient loading (Fig. 18.21B; Kemp *et al.*, 2005).

There is also evidence that N and P enrichment can significantly alter coastal ecosystems through changes in trophic structure that are not related to degradation of benthic habitat. With coastal eutrophication N and P loading tends to increase more rapidly than Si inputs, thereby resulting in decreasing Si:DIN ratios, limiting diatom growth and allowing smaller algal cells to dominate (e.g., Turner, 2001). The preponderance of smaller food particles reduces the efficiency by which primary production is transferred to herbivorous zooplankton and tends to increase the relative fraction of phytoplankton production that sinks to the benthos or enters the pelagic microbial loop (Kitchell and Carpenter, 1993). In addition to declining Si:DIN ratios, another mechanism causing a larger fraction of phytoplankton production to shift from zooplankton grazing to microbial degradation with nutrient enrichment involves predation-limitation on the growth of herbivore populations (e.g., Kemp *et al.*, 2001). Modeling studies suggest that this shift from metazoan grazers to microbial decomposers may be a general feature of all pelagic food-webs where exploited fisheries cause strong top-down control (Brooks *et al.*, 2005). Indeed, many investigators provide evidence to suggest that eutrophication tends to cause this shift from herbivorous grazing food-chains to microbial pathways (e.g., Baird *et al.*, 2004). Although detailed mechanistic understanding of these trophic responses to nutrient enrichment are generally lacking, recent evidence suggests that some systems may be currently experiencing Caddy's third stage (e.g., Yamamoto, 2003).

6.2. Effects of estuarine animals on nitrogen-budgets and cycles

In addition to being affected by N-loading to coastal waters, many animal populations in estuaries and other environments markedly influence the balance and cycling of N and other nutrients (Kitchell *et al.*, 1979). For example, respiration and excretion by Atlantic menhaden traveling in large schools can significantly deplete oxygen and increase ammonium concentrations in estuarine waters (Oviatt *et al.*, 1972). In pelagic estuarine mesocosm experiments, fish have been shown to enhance phytoplankton growth both through top-down effects on zooplankton grazing and through bottom-up effects of nutrient excretion (e.g., Micheli, 1999). In most cases, however, such large direct effects of fish on estuarine N dynamics are confined to dense schools of herbivores or planktivores. In some estuaries with productive fisheries, harvest can account for a modest loss (≈2–8%) of N inputs to the system, and an additional N sink of similar, or even larger magnitude, may be associated with emigration of fish using the estuary as a seasonal feeding ground (e.g., Boynton *et al.*, 1995; Deegan, 1993).

Benthic invertebrate populations can also influence N cycling in estuarine environments. As discussed earlier in this chapter, benthic invertebrates living as deposit-feeding infauna can influence nutrient cycling both through ventillation and bioturbation of sediments and through direct excretion and related metabolic processes. Reefs and other dense populations of benthic filter-feeders can, however, exert substantial influence on estuarine N cycling and transformation processes via a range of mechanisms. It is well established that filtration by clams, mussels and oysters can substantially reduce phytoplankton populations in overlying waters (e.g., Cloern, 1982). In many estuaries, native benthic filter-feeding populations have been depleted to levels that currently have little impact on plankton dynamics (e.g., Newell, 1988). In other estuaries, however, non-native species of benthic bivalves have grown to sufficient densities to readily control phytoplankton abundance in overlying waters (Cohen *et al.*, 1984). In a few coastal systems, healthy bivalve populations can still control plankton communities under certain hydrologic conditions (e.g., Møhlenberg, 1995). Similar densities of benthic bivalves, such as hard clams, have been shown to cause significant increases in rates of sediment N cycling through both direct excretion and increased turn-over of organic matter (e.g., Doering *et al.*, 1987). Under extreme conditions of intense benthic filtration associated with commercial culture, rates of N and P recycling can be greatly enhanced (e.g., Souchu *et al.*, 2001) stimulating growth of benthic macro-algae (e.g., Rafaelli *et al.*, 1998). In contrast, the eastern oyster, which maintains high clearance rates that are relatively independent of food concentration, produces large amounts of particulate N and P as psuedofeces (Newell *et al.*, 2004). Much of this pseudofecal material is deposited initially in shallow areas, where it supports enhanced production of deposit-feeding animals and increased nutrient burial (Newell *et al.*, 2004). In addition, recent experiments indicate that such oyster bio-deposits may stimulate N_2 loss via coupled nitrification-denitrification (Newell *et al.*, 2002). Although many questions remain, we are beginning to understand how heterotrophic organisms from bacteria to fish are linked together through diverse pathways and relationships in estuarine N cycles.

7. SUMMARY AND FUTURE DIRECTIONS

We indicated at the beginning of this paper that the last two decades have seen significant advances in understanding many aspects of N in estuaries. Scientific progress is, perhaps, difficult to comprehend on times-scales less than decades because the slow, incremental adaptation to new or refined ideas tends to mute our sense of progress. Our review of the estuarine N literature from the twenty years since the publication of Carpenter and Capone (1983) has revealed important new developments in this field. A vastly expanded pool of measurements, ranging from simple N concentrations to far more sophisticated rate measurements, supports this conclusion. Improved measurement techniques and wider access to new instrumentation have also contributed to this progress. Twenty years ago, there were simply too few observations reported to develop robust generalizations about spatial and temporal patterns and controls on N cycling processes. In addition, a matured understanding of nutrient-limitation of primary production in estuarine systems during this time has contributed to development of science-based nutrient and eutrophication abatement programs in many estuarine systems.

Synthesis of these diverse observations into useful estuarine models of N transport, transformation, assimilation, and storage has, however, made less progress during this time period (e.g., Cloern, 2001; Nixon *et al.*, 1996). Using the broad, ecosystem scale perspective adopted in this paper, we emphasize the continued need for more rate measurements, data syntheses and predictive models of estuarine N cycling. Most estuarine research and monitoring programs have focused on measuring N concentrations, with much less emphasis on rate measurements that are needed to assess system dynamics. For example, N loss terms due to burial, denitrification and export are rarely measured at annual time-scales for whole systems, while other key rate processes such as primary production rates of benthic autotrophs have been virtually ignored until very recently (Chapter 23 by McGlathery, this volume). An important goal is to find ways to incorporate rate measurements into long-term, system-wide monitoring programs rather than relegate such measurements to research programs focused at smaller and shorter scales. For many coastal systems worldwide, vast and expanding water quality data sets call for integrated synthesis focused on N cycling and related issues. Nutrient budgets represent one type of synthesis that requires a variety of processes to be linked for computing the sources and fates of N in estuaries. The challenge is to develop multi-year N-budgets for diverse estuarine systems using consistent protocols (e.g., Gordon *et al.*, 1996). Future comparative analyses of these budgets will contribute to a deeper understanding of physical, geological and climatological controls on estuarine N dynamics.

Finally, we suggest that innovative conceptual, analytical and forecasting models need to be developed and tested against field and experimental observations. Recent conceptual schemes proposed to describe and explain ecological interactions associated with estuarine eutrophication (Cloern, 2001; Kemp *et al.*, 2005) need to be quantified toward the goal of developing reliable numerical models for testing our scientific understanding and for providing useful forecasts for estuarine nutrient management. It is particularly important that conceptual models relating N-loading to fish production and harvest (e.g., Caddy, 1993; Nixon and Buckley, 2002) be quantified, tested and improved to support ecosystem based management of water quality and fisheries. It is clear that current estuarine science is rich with empirical observations but relatively poor on integrated understanding. Nowhere is the need to apply such integrated, predictive scientific knowledge more severe than in the world's estuarine regions, where disturbance associated with densely populated human societies threatens the quality of these productive ecosystems.

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